IMPACT OF HIGH TOTAL DISSOLVED SOLIDS, MANGANESE AND NICKEL IONS ON THE HYBRID ZERO-VALENT IRON TREATMENT SYSTEM

A Thesis

by

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ABSTRACT

Wet Flue Gas Desulphurization (FGD) is an air pollution control device that scrubs sulfur oxides from the flue gas of coal-fired electric power generations. The blowdown liquid stream from the FGD process is often contaminated with heavy metals, which requires advanced treatment for compliance with environmental regulations. To reduce water usage, power plants have steadily raised water recirculation cycles in the scrubber, thus increasing the strength of the wastewater that often exceeds 30 g/L in total dissolved solids (TDS). Removing heavy metals from a complex matrix of high TDS is a challenging task. In this study, we aim to evaluate the hybrid zero-valent iron (hZVI) technology as a viable solution for managing FGD wastewater, specifically, focusing on wastewater with high TDS and/or high manganese and nickel concentrations. For the purpose, bench-top continuous-flow hZVI treatment systems were operated to treat simulated wastewater with designed compositions under controlled conditions to evaluate the impact of TDS on the hZVI system and its performance for removing Mn and Ni.

Tests showed that high TDS at 62 g/L mainly consisted of Cl^-, SO_4^{2-}, Na^+, Ca^{2+}, and Mg^{2+} in the simulated wastewater could initially decrease the hZVI media reactivity with respect to nitrate reduction, but the media could gradually adapt to high TDS and over time the negative impact of high TDS diminished. On a long-term operation, high TDS has no obvious impact on hZVI system performance. Dissolved silica, which was previously believed to decrease hZVI reactivity through its interactions with dissolved

Fe^{2+} and iron oxide surface, exhibited no additional impact on the hZVI system performance at high TDS conditions. High level of carbonate alkalinity, however, was a significant factor that could decrease the hZVI reactivity. This study showed that the hZVI system is effective for treating high TDS wastewater featuring high Cl^- and SO_4^{2-}, which represents a major advantage over the biological or certain physicochemical processes that are highly susceptible to background salt level.

This study also demonstrated that high concentrations of Mn^{2+} or Ni^{2+} may be removed by hZVI, but as more Mn(II) or Ni(II) was incorporated into the FeOx structure of the hZVI media, the reactivity of the media could be negatively affected. Mn(II) or Ni(II) could substitute Fe(II) and occupy certain lattices within the FeOx structure. Such substitution could alter the chemical property of the FeOx and decrease media reactivity. Both Mn^{2+} and Ni^{2+} removal were greatly affected by the concentration of Fe^{2+} (aq.). Residual Ni^{2+} (aq.) may be dictated by Fe^{2+} (aq.) following an equilibrium constant in the hZVI media system. Under typical hZVI system operation conditions at near neutral pH and in presence of aq. Fe^{2+}, high removal of large quantities of Mn^{2+} may be achievable, but not sustainable. However, the hZVI system could be operated under a Fe^{2+} deficient condition, which would allow the media to take in both Ni^{2+} and Mn^{2+} in substitute of Fe^{2+}, thus decreasing Ni and Mn to a very low level in the treated effluent.

This study has expanded our knowledge of hZVI media water treatment system for industrial wastewater treatment, in particular with applications involving extremely high TDS, dissolved Mn and Ni conditions.

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Contributors

This work was supervised by a thesis committee consisting of Professors Yongheng Huang, Anish Jantrania, Zong Liu of the Department of Biological and Agricultural Engineering and Professor Xingmao Ma of the Department of Civil Engineering.

All work for the thesis was completed by the student, under the advisement of Professor Yongheng Huang of the Department of Biological and Agricultural Engineering.

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NOMENCLATURE

AAS	Atomic Adsorption Spectroscopy
Al^{3+}	Trivalent Aluminum
Fe^{2+}	Ferrous iron, or divalent iron
Fe_3O_4	Magnetite
HCl	Hydrochloric Acid
hZVI	Hybrid Zero-Valent Iron
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
M	Molarity (moles/L).
Mn^{2+}	Divalent Manganese
NaOH	Sodium Hydroxide
Ni^{2+}	Divalent Nickel
NO_3^- - N	Nitrate as Nitrogen
ZVI	Zero-Valent Iron

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1. INTRODUCTION

The landscape of the energy industry is fast-changing over the last decade, which ushered in numerous innovations and adoptions of new technologies that help make our society more efficient and sustainable. The push for using renewable energy by governments, industries and general public has never been stronger. Today, renewable energy accounts for 15% of the electricity generation in the US in 2016 (EIA, 2017). Despite such transformation, fossil fuels-based electricity still accounts for 64% of the electricity generation out of the total 4 trillion kilowatt-hours in 2016 in the US (EIA, 2016). Fossil fuels such as coals and natural gases are still the basis upon which our society relies heavily. Mining, processing, and utilization of fossil fuels may result in the productions of various gas, liquid and solid wastes that, if not handled properly, may harm our environments and pose a risk to public health. How to use fossil fuels, coals in particular, more cleanly remains a top interest of the public. To protect the environment, federal and local governments have enacted various regulations that require the electric power industry to more effectively manage the wastes and mitigate the pollutions.

Coal, the major fuel for electricity generation around the world, has been under intensive public scrutiny for its environmental impacts for decades. Coal naturally contains various impurities such as sulfur, nitrogen, and many trace metals/metalloids. As coal combusts, it releases not only CO_2, a greenhouse gas, but also certain criteria pollutants such as SOx, NOx, HCl, and Hg that are regulated by the Clean Air Act in the US and around the world. Over the decades, various environmental technologies and

devices such as selective catalytic reduction (SCR) devices, electrostatic precipitator (ESP), sorbent injection, fabric filtration (i.e., the bag house), and flue gas desulfurization (FGD, or scrubber) technologies are increasingly incorporated into the ever more complex environmental control system in coal-fired power plants.

Reduction of SOx emission from coal combustion for environmental regulatory compliance can be achieved using various flue gas desulfurization (FGD) technologies. The FGD systems employ alkali solvents (such as hydrate lime or lime stone slurry) to react with SOx and scrub the pollutants from the flue gas stream. Depending on the amount of water utilization, the FGD systems can be classified into three categories, wet process, semi-dry process and dry process (Carpenter, 2012). Although the dry FGD processes produce less waste, the wet FGD systems are widely adopted due to its high efficiency (e.g., over 98% SO_2 removal) and other benefits such as Hg capture. As the wet FGD system operates, various contaminants/impurities in the flue gas, fly ash and sorbent materials naturally accrue in the wet slurry. As such, the liquid becomes "dirty" in the wet FGD system, which must be constantly removed as a blowdown and replenished with fresh water. The FGD blowdown water is often contaminated with heavy metals such as selenium, arsenic, and mercury, which requires advanced treatments for deep reduction of the concerned heavy metals in order to comply with the latest USEPA rules, e.g., the Effluent Limitation Guidelines for steam electric power industry (USEPA, 2015).

Over time the coal power industry recognizes the needs and benefits of reducing the volume of the wet FGD blowdown: First, plant could reduce consumption of fresh

water, which is a precious resource in many places. Second, it reduces the volume of FGD wastewater, thus the size and cost of the needed treatment system. Third, it also aligns well with the long-term goal and development trend of the industry toward realizing zero-liquid discharge (ZLD) in the future (IWC, 2016). Reduction of FGD blowdown could be achieved by increasing recycle rate of the wet stream, which is often controlled by the limiting concentration of Cl^- allowed in the wet system for corrosion prevention control. As the recycle rate increases, the volume of FGD wastewater decreases. Inevitably, total dissolved solids (TDS) in the FGD wastewater would increase significantly, for example, from 10 g/L to 50 g/L. The composition of TDS in the FGD wastewater varies from plant to plant, depending on coal type and lime/limestone sources as well as scrubber operations and controls. The increased strength and the high concentrations of various TDS ingredients could pose a major challenge to the FGD wastewater treatment—targeting heavy metals in a complex compositional matrix and decreasing them to a level as low as a few microgram per liter is not a small task.

The increasing strength of the FGD wastewater may affect the performances of existing FGD wastewater water treatment systems. Currently, there are two main technical options that can help power industry to comply with the ELGs rule of the USEPA. For the ELGs compliance, selenium removal represents the main technical constrain for system design. One approach employed by the industry is to have a dedicated biological treatment system (represented by the General Electric's ABMet® technology) for selenium removal in conjunction with other physiochemical processes to

removal other heavy metals such as using organosulfide sorbent to remove mercury. A newer and simpler technology that can remove all major heavy metal/metalloids of concern in a single treatment is the hybrid zero-valent iron (hZVI) technology. The ZVI/iron-oxide based technology was developed at Texas A&M University (Huang et al. 2012) and later commercialized by Evoqua Water Technology Inc. under the name of Pironox® Advanced Reactive Media Technology. The hZVI technology demonstrated high effectiveness in removing selenium, arsenic and mercury as well as most common heavy metals of concerned such as cadmium, chromium, nickel, lead, zinc, and vanadium in one process to very low concentrations in compliance with many of the most stringent regulatory effluent limits (Huang et al, 2013). As a pure chemical process, the hZVI technology has a major advantage in daily operation and management when compared to a biological + multiple physicochemical processes system. The hZVI system is also economically competitive for its limited chemical consumption and solid waste production.

The increasing strength of FGD wastewater could pose a challenge to both existing and emerging treatment technologies. In biological wastewater treatment, the activities of microorganisms could be greatly affected by salt concentration in the wastewater. It was reported that biological selenium removal systems such as GE Water ABMet® functioned poorly or even collapsed when TDS in wastewater exceeded certain thresholds. For the hZVI system, the removal of heavy metals, often in forms of dissolved oxyanions or metal cations, might also be affected by TDS as chloride, sulfate,

borate, and silicate ions may interact with iron/iron oxide media and interfere with the chemistry and kinetics responsible for selenium, arsenic and mercury removals.

The raw coal burned by the plant and the sorbent raw material such as limestone used in the wet FGD system could determine to a large degree the nature of the FGD wastewater. It has been observed at some power plants that when limestone rich of manganese is used, the FGD wastewater could accrue over 100 mg/L in dissolved Mn^{2+}. Among dozens of raw FGD wastewaters obtained from different power plants by our laboratory, our analyses showed that while most FGD wastewaters contains less than 5 mg/L in dissolved Mn concentration (i.e., Mn^{2+}), three FGD wastewater samples reported unusually high Mn^{2+} concentrations in excess of over 50 mg/L. Such high Mn^{2+} pose two challenges: First, although Mn is not considered a dangerous or toxic pollutant but rather a concern for its aesthetic/cosmetic effects, it must still be decreased to a certain limited (e.g., <3 mg/L) before discharge. Therefore, whether or not the hZVI system could effectively remove high concentrations of dissolved Mn will need to be evaluated. Second, the presence of a high concentration of dissolved Mn^{2+} (and its removal) could alter the chemistry of hZVI systems and thus might affect the overall effectiveness of the hZVI media in removing other main target contaminants such as selenium.

The objective of this study is to further evaluate how water quality variations would affect performance of the hybrid ZVI treatment system. In particular, we would like to assess how the increase in TDS in the FGD wastewater resulted from the operational change of a wet scrubber system could affect the reactivity of the iron/iron

oxide media of the hZVI system for contaminant removal. Secondarily, we aim to evaluate how certain water quality parameters such as high dissolved manganese and nickel would affect the performance of the hZVI system and how to control and operate the hZVI system to achieve high removal of Mn and Ni and limits their impact on the removal of the other key contaminants in the wastewater.

2. CHALLENGES OF FLUE GAS DESULFURIZATION WASTEWATER TREATMENT

2.1 Flue Gas Desulfurization System and the Wastewater Problem

Flue Gas Desulfurization is used primarily to control acidic gases such as sulfur oxides (SO_x) emissions from coal-burning industrial boilers, mostly importantly from coal-fired power plants. The FGD systems allow coals that have various sulfur content to be burned in an environmentally acceptable manner (Homolya et al, 1979). The most common type is wet FGD scrubber systems, among which the limestone forced oxidation and the lime or limestone inhibited oxidation system are the most installed systems in the industry (EPA, 2009). A typical wet limestone FGD system includes the limestone storage and supply device, an absorber tower, a dewatering system for harvesting the byproducts, and a wastewater treatment system (Carpenter, 2012). This process is depicted in Figure 2.1. The flue gas is fed into the absorber tower, where sorbent, prepared in form of slurry, is sprayed as a fine mist to mix with the flue gas. The acidic gases such as SO_2 react with alkaline sorbent (hydrate lime/limestone) to form gypsum ($CaSO_4$) and are subsequently captured and removed from flue gas. The sorbent slurry is recycled many times until exhausted. While the target acidic gases are stripped off the flue gas, other constituents in the flue gas including fly ashes particles, volatile heavy metal vapors such as mercury, arsenic, and selenium, could also be stripped off the gaseous phase and accrued in the sorbent slurry. A side stream of the slurry is diverted to the dewatering system, where the slurry is dewatered to produce a solid cake

that consists of primarily gypsum. The water generated from the dewatering system may be recycled back into the absorber; but a certain level of discharge (blowdown), balanced with fresh water replenish, must be maintained to limit the buildup of the total dissolved salts, chloride in particular, to a level harmful to the system equipment and its operation. The FGD wastewater, often high in TDS and laden with various heavy metals such as mercury, selenium and arsenic, must be treated properly before it can be safely discharged (Carpenter, 2009).

In 2015, the U.S.EPA finalized the first federal limits on the level of toxic metals for the FGD and other wastewater discharges from thermo-electric power plants (40 CFR Part 423), setting the regulatory base for all coal-fired power plants to comply with the stringent standards (Table 2.1.1). The volume of FGD wastewater was estimated ranging from 3.8 to 6.8 L/min per MW generation capacity (Stiegel et al, 2007). For a 1000 MW power plant, the FGD wastewater could be over 1000 gpm. FGD wastewater contains significant concentrations of chloride, TDS, nutrients, and metals, including bio-accumulative pollutants such as arsenic, mercury, and selenium (EPA, 2009). The exact composition of the FGD waste stream varies significantly depending on the types of the coal burned by the plants and the impurities in the lime/limestone materials used for the FGD systems. The types of the wet scrubber and their operational and control statuses could also affect the quality of the FGD wastewater.

Table 2.1.1 Long-Term Averages and Effluent Limitations and Standards for FGD Wastewater and Gasification Wastewater for Existing Sources. (USEPA, 2015)

Wastestream	Pollutant	Long-term average	Daily maximum limitation	Monthly average limitation
FGD Wastewater (BAT & PSES)	Arsenic (µg/L)	5.98	11	8
	Mercury (ng/L)	159	788	356
	Nitrate as N (mg/L)	1.3	17.0	4.4
	Selenium (µg/L)	7.5	23	12
Voluntary Incentives Program for FGD Wastewater (BAT only)	Arsenic (µg/L)	[a] 4.0	[b] 4	([c])
	Mercury (ng/L)	17.8	39	24
	Selenium (µg/L)	[a] 5.0	[b] 5	([c])
	TDS (mg/L)	14.9	50	24
Gasification Wastewater (BAT & PSES)	Arsenic (µg/L)	[a] 4.0	[b] 4	([c])
	Mercury (ng/L)	1.08	1.8	1.3
	Selenium (µg/L)	147	453	227
	TDS (mg/L)	15.2	38	22

[a] Long-term average is the arithmetic mean of the quantitation limits since all observations were not detected.

[b] Limitation is set equal to the quantitation limit.

[c] Monthly average limitation is not established when the daily maximum limitation is based on the quantitation limit.

2.2 FGD Wastewater Treatment Technologies

Up until the turn of the 20th century, most coal power plants discharged FGD wastewater into settling ponds, often along with other by-products of coal power generation such as fly ash (Mehnert et al, 1996), thus resulting numerous waste storage sites commonly known as gypsum ponds and ash ponds. These practices, however, are no longer permitted under the new ELGs regulation (the USEPA, 2015). The pond disposal method was favored due to its simplicity as particulates can be removed by gravity settling over time without using chemicals. Such simple physical treatment, however, has minimal capability in removing dissolved pollutants. More importantly, many of these ponds are unlined, thus increasing the risks of contaminants leaching into groundwater. To mitigate the risk posed by the FGD wastewater, the U.S.EPA set much stringent effluent discharge limits for the steam electric power generation industry, which outlaw the use of pond and requires advanced treatment for deep reduction of the major concerned contaminants such as Hg, Se, As and nitrogen in the FGD wastewater discharge.

Over the years, great efforts and resources have been devoted by the government and industry to evaluate existing technologies and to develop new technologies that could cost-effectively treat the FGD wastewater for compliance. The main technical challenge lies in selenium and mercury removal. For selenium removal, anaerobic biological treatment was considered most promising. Among the industrial companies with a focus on developing biological selenium removal technologies, GE Water led

with the development of the ABMet® processes. For mercury, however, the conventional approach is the use of sulfide reagent to precipitate dissolved mercury through the formation of HgS that is extremely low in solubility. The viability of constructed wetlands, with the potential advantages of low maintenance and limited chemical consumption, has also been explored; but its practicability is significantly constrained due to the susceptibility of microorganisms to temperature variations and other environmental disruptions (EPA, 2009; Chu, 2006). Other technologies that had been evaluated include iron cementation, reverse osmosis, various sorption media, ion exchange, and electro-coagulation. These technologies might each have a specific niche of application within the FGD field, but in general is not considered a real and viable solution for the power industry (Chu, 2007). Zero-valent iron (ZVI) as a reducing agent was also evaluated by many researchers as a promising media for selenate reduction and removal, but after many failures that were attributed mainly to the ZVI surface passivation problems, ZVI technology was virtually delisted from the viable techniques by the power industry by 2010. The prospect of ZVI changed only when the surface passivation problem was solved later by the invention of the hZVI technology (see below).

In the course of developing the new ELGs rule for the electric power industry, the USEPA conducted extensive background research to gather information regarding the best available technologies (BAT) for the FGD wastewater treatment. It was determined that selenium removal and nitrate reduction could be achieved by biological treatment systems represented by GE ABMet®, while other metals such mercury,

arsenic and copper could be treated with a combination of physicochemical processes and reagents such as organ sulfide precipitation and conventional coagulation-precipitation processes. Therefore, the USEPA proposed at the time that a combination of multiple physicochemical processes in conjunction with a biological selenium treatment system might be the best available technology for the planned ELGs compliance.

2.3 Zero-Valent Iron Technology as a Potential Solution

Zero-valent iron (ZVI), or elemental iron, with a standard redox potential of E_0 (Fe^0/Fe^{2+}) = −0.44V (Shokes et al, 1999), is a versatile and effective reductant that can readily react with many environmental contaminants (refs). ZVI powder is relatively inexpensive and readily available in large quantities as an industrial material. Moreover, ZVI is non-toxic. Because of these potentials and advantages, extensive research has been conducted to develop ZVI-based techniques for environmental remediation applications, e.g., reducing heavy metals, and transforming chlorinated organic compounds into less or non-toxic variants of molecules (Fu et al, 2014). While redox reductions are considered as the main mechanism, ZVI media could also remove contaminants by surface adsorption and precipitation, or even oxidation under aerobic conditions where ZVI may help create certain radicals in the water through what is known as the Fenton reactions (Shen et al, 2013).

One major obstacle for the application of ZVI, however, is the rapid surface passivation problem: ZVI can be oxidized (i.e., corrode) rapidly once the media come

into contact with the target wastewater or soils, forming an iron oxide film that coats on the ZVI grain surface. Such iron oxide coatings are often chemically passive, thus the surface chemistry is impeded and the reactivity of ZVI is quickly lost (Fu et al, 2014). Many methods were proposed and evaluated with an aim to overcome this ZVI passivation problem: for examples, reducing the size of ZVI particles, binding ZVI onto other support materials, washing ZVI with acids or doping other metallic ions (Lu et al, 2012). Acid washing may remove the inert outer shell of ZVI and recover the ZVI reactivity, but the method significantly increases ZVI consumption and solid waste generation. Among these potential solutions, nano-scale zero-valent iron (nZVI) media received the greatest interest with extensive studies in the last decade (refs). With its high specific surface area, nZVI media naturally exhibits extremely high reactivity, which may enable rapid degradation and removal of contaminants; but on the other side, the excessively high reactivity of nZVI may significantly shorten the media lifespan as nZVI is consumed rapidly through its wasteful reactions with water and oxygen, which may also lead to fire and explosion hazard potentials. The nZVI approach may be technically effective, but economically unattractive as nZVI is significantly more expensive and also not available in large quantity due to the sophisticated production processes. Moreover, the nZVI particles may be difficult to be separated from the treated solution once reaction is completed (O'Carroll et al, 2013). Alternatively, binding nZVI onto supporting materials such as clay particles or activated carbon may facilitate media/water separation. It was reported that nZVI incorporated onto chitosan beads effectively removed heavy metals such as $Cr^{(VI)}$, $Cu^{(II)}$, $Cd^{(II)}$ and $Pb^{(II)}$ from

electroplating water with efficiency as high as 99.4%, but the economic feasibility was not clear (Liu et al, 2013).

In short, despite its great potential, the use of ZVI in environmental application is greatly constrained in the absence of a breakthrough solution to the ZVI passivation problem.

2.4 Hybrid ZVI Technology

Huang et al. (2003) discovered that adding Fe^{2+} into a ZVI system can maintain high reactivity of ZVI with respect to nitrate reduction despite the formation and presence of a substantial iron corrosion coating. Further studies discovered that externally added Fe^{2+} into a ZVI/nitrate system promotes the formation of a magnetite coating on the ZVI surface, which plays a key role in maintaining the reactivity of ZVI media. Magnetite (Fe_3O_4), a mixed Fe(II)-Fe(III) oxide with an inverse spinel structure, is a semiconducting material that possesses a metal-like electron conducting capability. Moreover, the magnetite formed in the ZVI/nitrate/Fe^{2+} system is non-stoichiometric in term of the ratio of Fe(II) to Fe(III), which creates lattice vacancies and contributes to high ion conductivity that is essential for rapid ZVI corrosion. A semiconducting model was proposed to explain the sustained high reactivity of ZVI when coated with a magnetite layer as its corrosion product. Subsequent studies further discovered that retention of the mature magnetite crystalline produced from the iron corrosion process as a discrete magnetite phase could further increase the ZVI system's reactivity as the magnetite crystalline could serve as the electron shuttle and provide additional reactive

surfaces where redox reactions could occur and contaminants like nitrate and selenate could be reduced and removed. These new understandings eventually led to the invention of the Hybrid ZVI/Fe_3O_4/Fe(II) (hZVI) reactive treatment system, which is featured with in-situ creating/maintaining a magnetite phase and augmenting the system with externally-supplied Fe(II) source to form a hybridized reactive media system. The effectiveness of the hZVI technology have been demonstrated in both laboratory and field tests in treating selenate, dissolved mercury, hexavalent chromium and arsenic-contaminated industrial wastewater, including mining drainage, refinery stripped sour water, oil & gas co-produced water and flue-gas-desulfurization wastewater from coal-fired power plants. The hZVI technology could be a cost-effective solution and meet many current and emerging industrial needs in water/wastewater treatment. In particular, it could help industries meet the most stringent effluent regulations for trace metals such as mercury, arsenic, and selenium. The bench-scale treatment prototype, with a capacity of treating 30 L FGD water per day, was successfully demonstrated in a five-week field test in 2009 at a power plant, consistently reducing selenate selenium from 2-4 ppm concentration to below 0.01 ppm and dissolved mercury from over 20,000 ppt to below 10 ppt (Huang et al. 2012). Currently, the technology has been commercialized by Evoqua Water Technology Inc. under the name of Pironox® Advanced Reactive Media Technology, which reported the first full-scale application of the hZVI technology for treating heavy metal contaminated-wastewater at a power plant site.

One important process for the hZVI system application is a procedure referred as "media preconditioning", which converts fresh ZVI powder into highly reactive and

sustainable hZVI media. In the laboratory, this process is accomplished by adding Fe^{2+} and nitrate to react with ZVI powder under controlled conditions to coat the surface of ZVI grain with magnetite coating and produce certain amount of discrete magnetite crystalline. In commercial applications, this media conditioning process could be achieved using a carefully-controlled aeration process with the presence of certain reagents. The main purpose of preconditioning is to change the surface condition of the ZVI media by coating a layer of magnetite on ZVI surface to form hZVI system. The mixture of ZVI, ferrous iron and nitrate reacts to form magnetite following Equation (1) (Huang et al, 2002).

$$NO_3^- + 2.82\ Fe^0 + 0.75\ Fe^{2+} + 2.25\ H_2O \rightarrow NH_4^+ + 1.19\ Fe_3O_4 + 0.5\ OH^- \qquad (1)$$

Equation (1) was slightly modified in this test, and the ratio of 1/0.7 is adopted for nitrate/ferrous iron since fresh ZVI naturally releases a small amount of ferrous iron as it reacts with water.

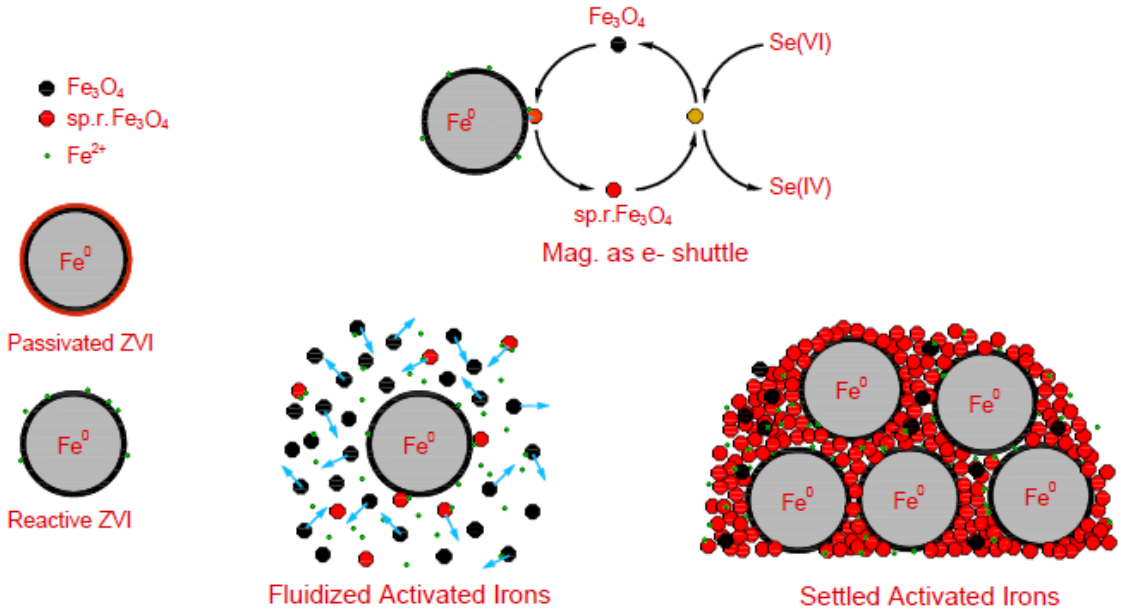


Figure 2.4.1 Graphical representation of the hZVI media system (also called the activated iron media) and its reactivity. Passivated ZVI is covered with non-reactive iron oxide coating on the ZVI grain. The presence of dissolved Fe2+ interact with the passive iron oxide coating and converts it into a reactive magnetite coating. The activated iron media consisted of three components: magnetite-coated ZVI, discrete magnetite crystalline, and dissolved or surface-adsorbed Fe2+. In a fluidized mode, discrete magnetite could harbor on ZVI grain surface and acquire e- to become super reactive magnetite, which could subsequently interact with contaminants (e.g., SeO42-) and transfer the e- to reduce SeO42-.

2.5 New Development and Trend Surrounding FGD Wastewater

Compliance with the new ELGs for the FGD waste stream is challenging in both technical and cost aspect for the power industry. The best available technologies proposed by the USEPA, i.e., a multiple physicochemical + biological treatment processes, is still far from an ideal solution. The system will be very complex, expensive

to build and operate, yet still not reliable due to the nature of a biological system and the complexity/variability of the FGD wastewater. In fact, multiple pilot tests showed that the current BAT would not guarantee plant's compliance with the ELGs regulation. When an electric plant cannot reliably treat their waste streams to the desired levels, ZLD is an attractive alternative (Perez et al, 2016). The main goal of a ZLD plant is to treat the liquid waste stream until it is clean enough for reuse in the plant, creating a closed loop for water usage. The main challenge with ZLD is that the cost may not be competitive enough compared to the physical/chemical plus biological treatment costs (Perez et al, 2016). One common solution to achieve ZLD is to concentrate the waste stream through evaporators and then use a crystallizer to extract the dissolved solids for disposal or blend the evaporator brine with fly ash in lieu of crystallization. Since one of the main driving forces of the cost in a ZLD plant is the hydraulic flow rate, it is commonly accepted that flow reduction is one of the key processes to make ZLD costs competitive (Higgins et al, 2016). The result of flow reduction is a more concentrated waste stream, which could potentially cause corrosion and other unexpected problems. Many studies have been done recently in this area to address the main issues with implementing ZLD, especially the high cost. Methods proposed include adding clarifiers, settling tanks, additional pretreatments, and special filters (Higgins et al, 2016). For ZLD, how to handle the concentrated brine and the salt wastes laden with heavy metals has not been addressed adequately by the industry. Simple spraying the concentrate on fly ash may risk causing secondary pollutions when the unsecured heavy

metals escape into the environment. Ideally, it will be safer to treat the wastewater to remove heavy metals before sending to the ZLD processes.

Another emerging trend in the FGD industry is higher recirculation cycles. Water used in the FGD process is discarded once chlorides reach 5000 mg/L, but more plants choose to recirculate the water until reaching 20,000 mg/L for the benefits of reducing fresh water usage and wastewater production. This produces similar problems as in ZLD, because concentrated waste streams may be incompatible with existing treatment technologies (Córdoba, 2015). Treatment technologies, therefore, must adapt to the demands of the industry, staying relevant and viable to the waste stream characteristics that come with this trend.

2.6 Manganese and Nickel in Wastewater and the Treatment Technologies

Manganese, a transition metal right next to iron on the periodic table, can also be found in some FGD waste streams. Manganese is more of a problem in drinking water, especially ground water. Although EPA does not regulate manganese in the primary standards for drinking water, it set a secondary maximum contaminant levels (SMCL) for Mn at 0.05 mg/L. Oxidation is the most commonly used method for removing Mn by oxidizing dissolved Mn^{2+} into MnO_2, a precipitate that can be filtered mechanically (Aziz et al, 1992). The oxidation-filtration technologies include aeration-filtration, chlorination filtration, and potassium permanganate-manganese green-sand filtration, with aeration as the recommended method for higher concentrations of manganese to save on chemical consumption, and chlorination for lower levels of manganese due to

time and cost effectiveness (Wong et al, 1984). Although it is a well-established method, with numerous industrial facilities built in Germany and the United State in the 19th century, their extraction mechanisms have not yet been completely understood (Mouchet, 1992). Little work has been published on removal of manganese in a zero-valent iron system. The presence of manganese, along with the assortment of other chemicals in FGD waste streams makes it difficult to predict the behavior and impact of manganese within the hZVI system.

Nickel, on the other hand, cannot be easily removed like manganese through aeration. Nickel's main presence comes from industrial processes, especially from electroplating processes. It is recognized by the World Health Organization to be hazardous and regulated in the United States by the EPA at a maximum contaminant limit (MCL) of 0.1 mg/L for drinking water and 4.1 mg/L for electroplating process wastewater effluent. Many techniques have been developed for removing nickel, such as adsorption, chemical precipitation, ion exchange, filtration, membrane separation, and reverse osmosis. Adsorption is widely adopted as it is cost-effective and simple (Kandah et al, 2007). Studies on adsorbents ranging from carbon nanotubes to biological materials such as seaweeds, crab shell, dried aerobic activated sludge, sponges, activated carbon, even moss peats showed their effectiveness in nickel adsorption (Ho et al, 1995). Some bio-sorbents have unique affinity in capturing heavy metals such as nickel. As an example, the crab shells are reportedly capable of taking in roughly 20 mg nickel per g sorbent in a 100mg/L nickel condition; the crab schells, however, requires extensive pretreatment before being used. The crab shells were acid washed for 4 hours with 0.1 M

HCL, then rinsed with distilled water and dried. This media has shown to be able to be regenerated as well, with elution efficiencies greater than 99.1% in the study (Vijayaraghavan et al, 2004). Highest nickel adsorption rate reported at the time of writing is one with nano-ZVI, achieving 0.13g/g (Li et al, 2006). However, in this study, it was reported that adsorption is not the only mechanism behind nickel removal, but reduction as well. Nickel is one of the heavy metals that have not been fully explored for its relationship with the ZVI, and considering the hZVI system's higher reduction capability, it is possible that hZVI system could be a low cost technology for nickel reduction.

3. EFFECT OF HIGH TDS ON HYBRID ZVI TREATMENT SYSTEM

3.1 Research Objectives and General Approach

As discussed and explained in Chapter 2, one objective of this study is to evaluate how the exceptionally high total dissolved solids in the target wastewater may affect the reactivity of the hZVI media and the overall performance of the hZVI system. For the purpose, bench-top hZVI treatment systems were operated to continuously treat synthetic wastewater with designed composition matrix and characteristics on a relatively long-term operation base. Nitrate was used as the main indicator contaminant, and its reduction rate and efficiency by the treatment system was used to evaluate the reactivity of the hZVI media.

3.2 Bench-top hZVI Reactor Treatment System

Two bench-top hZVI treatment systems, each consists of one single-stage fluidized bed reactor, were set up for this study. The two systems were operated in parallel throughout the test period. One hZVI system was operated to evaluate system performance for treating synthetic wastewater with a designed composition and qualities such as TDS or other conditions, while the second system was operated as the baseline control for comparison. Each hZVI reactor measures 12 L of total volume including a 6 L inner mixing zone and a 6 L outer settling zone (Figure 3.1). An overhead electric stirrer with a three-pitched blade propeller of 3.0 cm in diameter stirring at 1750 rpm was used to provide mixing in the reactor. The mixing power was sufficient to fluidize

and circulate the hZVI media along with the wastewater and reagent feeds in the inner reaction zone. The synthetic wastewater and the needed chemical reagents were fed to the mixing zone in the reactors using peristaltic pumps (Masterflex, Cole-Palmer). The flowrate of influent was set at 1.0 L/hr, which translated into a hydraulic retention time (HRT) of 6 hour in the reaction zone. The treated wastewater would enter the settling zone where the supernatant would overflow as the treated effluent and the solid media would settle and return to the reaction zone.

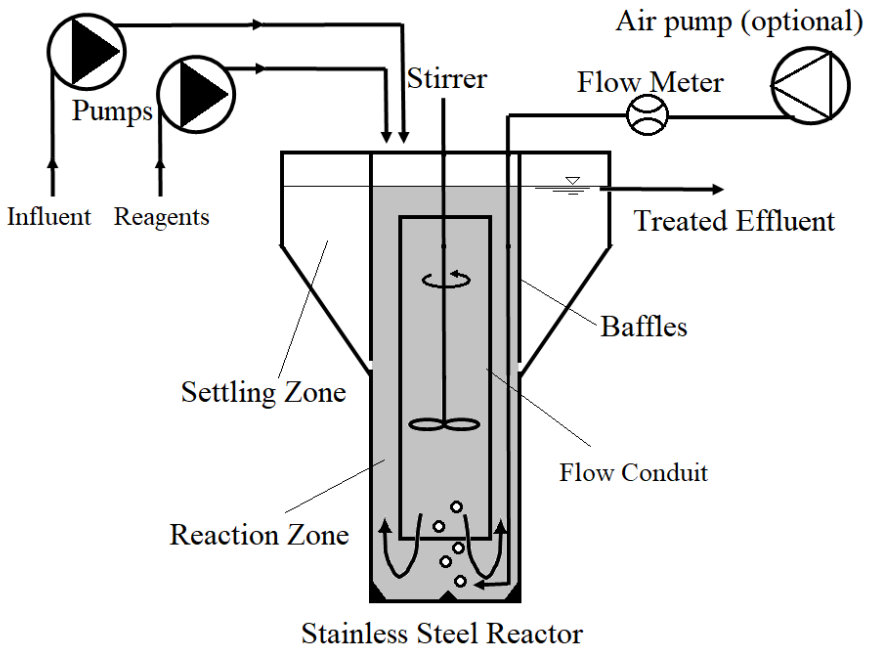


Figure 3.2.1 Schematic of the bench-top hZVI treatment system.

3.2 Materials

Industrial grade ZVI source (Hepure Technologies LLC) was used in this study, which reported a particle size of passing 325 mesh sieves, corresponding to a nominal diameter of <0.044 mm. Fe^{2+} solution, which was used as a reagent, was prepared from iron chloride tetrahydrate (Beantown Chemicals, >98% in purity). 6 N HCl solution (J.T. Baker) was added at 5 mM into the Fe^{2+} solution. Nitrate was prepared with sodium nitrate (Alfa Aesar, 98%+). Mg^{2+} was prepared using magnesium sulfate anhydrous (VWR, USP grade). Ca^{2+} was prepared using calcium chloride anhydrous (VWR, USP grade). SO_4^{2-} was prepared with sodium sulfate anhydrous (VWR, ACS grade). Cl^- was prepared using commercial non-iodized potable salt purchased from a local Walmart

store. Dissolved silica was prepared using sodium silicate (meta) (Aqua Solutions, reagent grade). Bicarbonate was prepared using sodium bicarbonate (VWR, ACS grade). Deionized water produced from a Barnstead E-Pure system was used for preparing all reagent solutions. RO water or tap water was used to make synthetic wastewater by adding designed amounts of selected salts and pH was adjusted to 7.

3.3 Sampling and Analysis

Influent and effluent of the hZVI treatment system were sampled daily. With an HRT=6 hr, this sampling frequency equates to one sample for every four HRTs. Influent samples were directly obtained from feed tank. Treated effluent samples were drawn with a 60 mL plastic syringe from the settling zone. The samples were filtered through 0.45 μm syringe filters into polyethylene bottles, which were capped and stored for various analyses. The USEPA approved methods were employed to analyze ferrous iron, dissolved silica and nitrate according to Standard Methods for the Examination of Water and Wastewater (ref?). Dissolved Fe^{2+} was determined using the phenanthroline colorimetric method (Method 3500-Fe B). Dissolved silica was determined using the molybdosilicate method (Method 4500-SiO_2 C). Nitrate was determined using the ultraviolet spectrophotometric method (Method 4500-NO_3-B). Nitrate was also quantified using the ion chromatographic method on a Dionex DX-500 IC system with an IonPac AS 22 separation column. The IC method reports a detection limit of about 0.05 mg/L for nitrate as N. All nitrate concentration are reported as N in this study. pH was measured using a Thermo Orion 2 star pH meter.

3.4 Compositions of the Synthetic Wastewater

This study is to characterize the effect of high TDS on nitrate removal in a hZVI system. As nitrate is a proven contaminant that can be reduced by the hZVI system (Huang et al, 2013), it was chosen to serve as the performance indicator for the reactivity of the hZVI system and the means to measure the impact of TDS on the hZVI system. Synthetic wastewater used in this study is based on typical composition of a real high strength FGD wastewater (Perez et al, 2016; Fonseca et al, 2016). Chloride was set at 35,000 mg/L, which was selected to represent the extreme condition when a plant maximally recirculates the water for repeated uses. Sulfate was controlled at 3000 mg/L, magnesium at 600 mg/L, and calcium at 300 mg/L. Sodium ions were added to increase the TDS to be around 62.1 g/L. Influent water was prepared using RO water or tap water. Influent's pH was adjusted to 7.00±0.05 using 6 N HCl.

3.5 Operation and Control of the hZVI Treatment System

The tests for TDS' effect on the performance of hZVI for nitrate removal were carried out in four separate runs (Run#1 to #4) designed to evaluate the combine impacts of high TDS with RO water, tap water, silica, and bicarbonate as the variables. Each run started with new media and lasted roughly a month. To convert ZVI to hZVI, 900 g of ZVI, 0.12 mol $NaNO_3$ (10.2 g) and 0.084 mol $FeCl_2$ were added into the reactors and react in batch mode for 24 h to complete the media preconditioning. At the end of preconditioning, sample was taken and analyzed to verify that all nitrate had been reduced by ZVI, which would resulted in about 20 g of ZVI being consumed to produce

about 30 g of magnetite. For Run#1, the influent was prepared by dissolving selected salts in RO water that has a TDS of 62.1 g/L with the composition described before (62.1 g/L). Nitrate, the performance indicator, was added into the influent feed at a level of 1.5 mM and later raised to 3.0 mM on the 20th day. Fe^{2+} solution as the essential reagent for hZVI was fed at 1.0 mM in the reactor and later increased to 2.0 mM as nitrate dosage increased. Run#2 was conducted under the same condition and procedure except that the influent was prepared with local tap water from College Station, Texas (Table 3.5.1), which was sourced from groundwater that contains constituents like silica and bicarbonate. Switching from RO water to tap water was meant to evaluate the effect of high TDS under a more complex water matrix. Once the effects of tap water were established, two more tests were conducted to pinpoint the source of the negative impacts. Run#3 was conducted similar to Run#1 except that the influent was spiked with dissolved silica at a concentration of 40 or 80 mg/L (15th day). Run#4 was conducted similar to Run#1 except that the influent was spiked with bicarbonate at a level of 400 mg/L to match the bicarbonate concentration found in the tap water in Run#2.

Table 3.5.1 Characteristics of tap water quality of the city of College Station (retrieved on December 17, 2017, from http://www.cstx.gov/Modules/ShowDocument.aspx?documentid=24513)

Year Sampled	Substance	Detected Levels	Units	Limit
2014	Alkalinity - Phenolphthalein (as CaCO3)	14	mg/L	No recommendation
2014	Alkalinity (Total)	390	mg/L	No recommendation
2014	Bicarbonate	442	mg/L	No recommendation
2016	Calcium	3.26	mg/L	No recommendation
2014	Carbonate	17	mg/L	No recommendation
2014	Chloride	57	mg/L	300
2016	Copper	0.005	mg/L	1
2014	Diluted Conductance	966	µmhos/cm	No recommendation
2014	Fluoride	0.48	mg/L	2
2016	Iron	0.022	mg/L	0.3
2016	Manganese	0.0085	mg/L	0.05
2014	pH	8.4	N/A	>7.0
2016	Potassium	1.85	mg/L	No recommendation
2016	Sodium	222	mg/L	No recommendation
2014	Sulfate	8	mg/L	300
2014	Total Dissolved Solids	544	mg/L	1,000
2016	Total Hardness as CaCO3	8.14	mg/L	No recommendation

3.6 Impact of High TDS on hZVI System Performance

Results from treating RO water-based synthetic wastewater

In Run#1, the two hZVI systems was operated continuously for 4 weeks, with Reactor#1 used as the baseline control for treating RO water spiked with nitrate (low TDS) and Reactor#2 for treating synthetic wastewater prepared from RO water spiked with high TDS and 1.5 mM nitrate. The baseline reactor performed as expected from previous reports, reducing nitrate from 21 to below 1 mg/L consistently. The reactor with high synthetic TDS only reduced nitrate down to 3 mg/L on the first day of

operation versus 0.3 mg/L on the baseline, but nitrate reduction improved over time to below 0.5 mg/L (Figure 3.6.1). The two reactors were virtually indistinguishable after the first week in term of nitrate reduction. The nitrate removal remained stable in the following two weeks. At day 20, nitrate concentration was doubled in the influent. Over 95% nitrate removal was still observed for both reactors, while the high TDS reactor outperformed the baseline reactor by a small margin. This is consistent with the previous reported results (Huang et al, 2004). A decrease in performance as observed initially was expected as the hZVI system included an adsorption component and high TDS may impede it (Hayes et al, 1988). Hayes reported that certain anions, such as phosphate or selenite, will remain largely unaffected by the ionic strength below 1M when bonding to oxides as they possess a stronger bond. It could be understood that as time passes the hZVI surface composition changes in a fashion that favors nitrate to bond with the oxide surface, thus the observation of similar removal rate after one week of reactor operation.

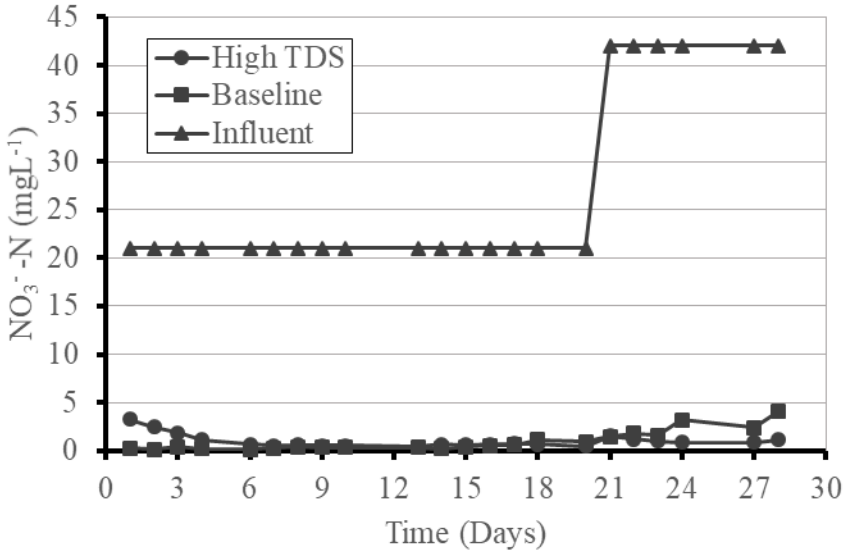


Figure 3.6.1 Nitrate removal over time in Run#1, in which Reactor#1 (baseline) was fed with RO water and Reactor#2 with RO + high TDS synthetic wastewater. High TDS had some initial impact on the system performance, but such impact diminished over time and both reactors achieved over 95% nitrate removal rates for most of the test duration.

Results from treating TAP water-based synthetic wastewater

In Run#2, the two hZVI systems were operated in ways similar to Run#1 except that tap water was used to replace RO water in the influent. Overall, the system performed worse than Run#1 with respect to nitrate removal, achieving about 90% nitrate removal vs. > 95% removal in Run#1 with RO water. Again, reactor treating influent with high TDS did not seem to have any distinguishable difference on the performance when compared to the baseline reactor without the TDS content over the course of 3 weeks of operation (Figure 3.6.2). Also, the residual nitrate level was

essentially unchanged after doubling the nitrate in the influent at day 21, suggesting that the tap water adversely impact the nitrate removal mechanism largely at lower concentrations, or polishing stages of the hZVI process.

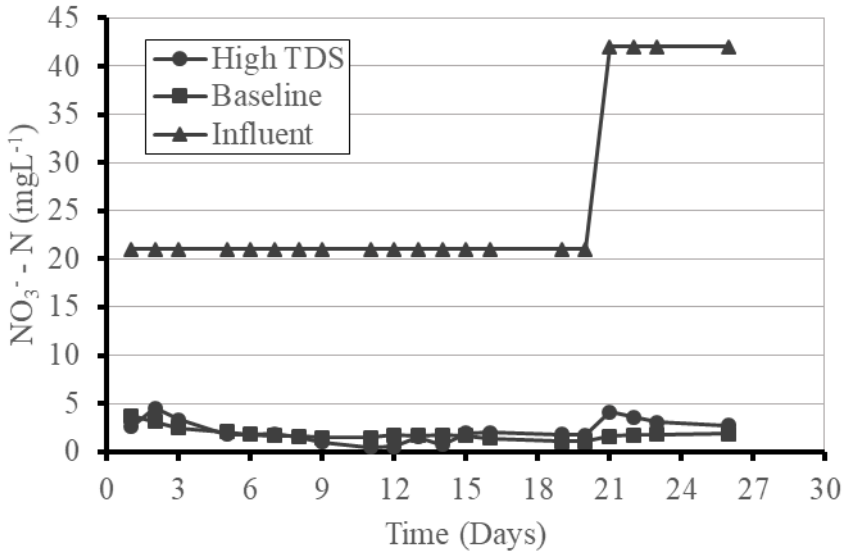


Figure 3.6.2 Nitrate removal over time in Run#2, in which the two hZVI systems were operated to treat synthetic wastewater with tap water + nitrate only (baseline) and with tap water + TDS + nitrate (high TDS). The results showed that high TDS has no obvious impact on nitrate reduction under the test conditions.

Results from treating synthetic wastewater with dissolved silica

Comparing results from Run#2 with Run#1, it could be inferred that that certain properties or constituents in tap water has negative impacts on the hZVI system. The list included chloride, sulfate, nitrate, calcium, magnesium as well as dissolved silica and borate. Most of these constituents had already been tested earlier for their impact on hZVI media reactivity.

Run#3 was conducted with aim to isolate the cause of such impacts in tap water. Since silica was present in a significant amount in the local tap water, naturally, it became the first target compound of interest. Dissolved silica was also one of the major constituents of the FGD wastewater (Huang et al, 2013). Run#3 was operated in ways similar to Run#1 except that dissolved silica was added into the synthetic wastewater at 40 or 80 mg/L. Nitrate removals in Run#3 were very similar to that of Run#1, as shown in Figure 3.6.3. Several unexpected spikes can be observed, but those seem to be an abnormality, likely due to operational or mechanical problems, as nitrate removal quickly recovered to a typical level. In consideration of the fact that dissolved silica was added in this test at double or quadruple concentrations of that of the tap water, little difference in nitrate removal between Run#3 and Run#1 suggested that dissolved silica was not the main contributor to the adverse impacts on the hZVI system by tap water. The residual dissolved silica level in the effluent was also consistently reduced to below 2 mg/L (over 95% removal) throughout the test, which was also consistent with the results reported from a field test with actual FGD wastewater (Huang et al, 2013).

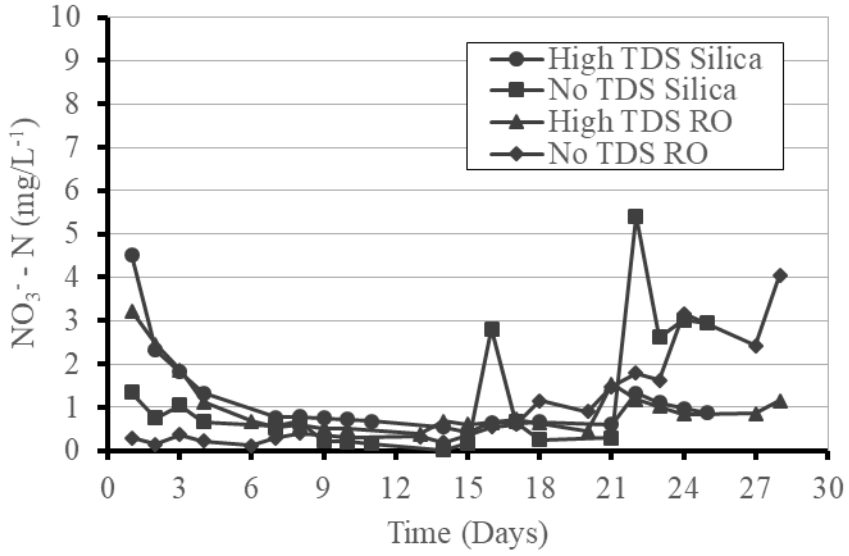


Figure 3.6.3 Nitrate removal over time in Run#3, in which the two hZVI systems were operated to treat synthetic wastewater with RO water + silica + nitrate (no TDS silica) and with RO water + TDS + silica + nitrate (high TDS silica). Results from Run#1 were added for comparison. The results suggested that dissolved silica is not main factor in tap water responsible for lower hZVI system performance with respect to nitrate reduction.

Results from treating synthetic wastewater with bicarbonate

Run#4 was conducted to evaluate the impact of bicarbonate as a suspected factor responsible poorer hZVI performance in treating tap water based synthetic wastewater. Bicarbonate (HCO_3^-), a primary constituent of alkalinity in water, could bind with dissolved Fe^{2+} and interfere its interaction with the reactive surface of the hZVI media. Bicarbonate interferes with adsorption of many compounds including nitrate (Zhan et al, 2011). Bicarbonate was identified to be present in large quantities in the tap water of College Station (Table 3.5.1). For the test, 400 mg/L bicarbonate, similar to that found in

tap water, was spiked in synthetic wastewater prepared with RO water + TDS + nitrate. Run#4 test results closely mirrored those observed in Run#2 with tap water-based wastewater (Figure 3.6.4). When nitrate concentration was doubled at Day ??, the hZVI systems behaved similarly: for the reactor treating high TDS wastewater, residual nitrate level increased initially after nitrate spike, but gradually returned to a lower level. Run#4 results suggest that bicarbonate is the main constituent in tap water that contributes to the decrease in the hZVI system reactivity. Bicarbonate might interfere with adsorption of ions such as nitrate onto the reactive surface site on iron oxides and thus lowering the overall reactivity of the hZVI system for nitrate reduction. Further investigation in the exact mechanisms and kinetics will be required to develop in depth understanding of the underlying mechanism.

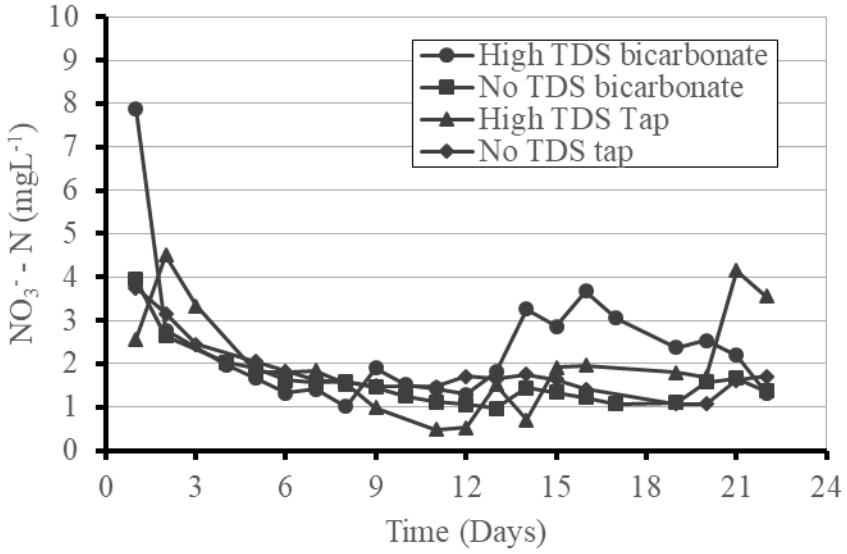


Figure 3.6.4 Nitrate removal over time in Run#4, in which the two hZVI systems were operated to treat synthetic wastewater with RO water + bicarbonate + nitrate (no TDS bicarbonate) and with RO water + TDS + silica + nitrate (high TDS bicarbonate). Results from Run#2 were added for comparison. The results suggested that bicarbonate is a key factor in tap water responsible for lower hZVI system performance with respect to nitrate reduction.

Discussion

The high level of TDS itself does not affect the hZVI system adversely on a long term basis in all of the tests conducted in this study. There was effect observed in the beginning of Run#1 with RO-based wastewater and in Run#4 after doubling the nitrate loading on the bicarbonate test. This behavior resembles that of a “lag” phase which are characteristic of biological systems, but would not be relevant in the hZVI system as it is a purely chemical process. Without additional in-depth investigations, however, it is difficult to pinpoint the underlying chemistry responsible for the repeatedly observed “disruption-then-recovery reactivity” that was associated with major change of

composition in wastewater influent. Reduction of nitrate by the hZVI media occurs on the FeOx-liquid interface, which requires the binding of nitrate onto certain redox reactive sites on the iron oxide surface. The presence of anions such as sulfate and chloride could compete with nitrate for surface adsorptive sites. Therefore, it is not reasonable that high TDS could slow down the overall reaction. Literature reports may provide clues for explanation. Adsorption of selenite and selenite on goethite and hydrous ferric oxide was found to be greatly affected by the ionic strength above 1.0 M (Hayes et al, 1988). The ionic strength of the synthetic high TDS influent was around 2.2 M, therefore, it was predictable that adsorption of nitrate onto the iron oxide surface could be greatly affected in the presence of high Cl^- and SO_4^{2-}, thus lowering the reactivity of hZVI media. However, the more challenging and unanswered question is why and how over time the ZVI media reactivity with respect to nitrate reduction could gradually recover over time. Since the influent water is unchanging, the hZVI media should be the source of the change that is responsible for improving nitrate removal capacity. In the continuous-flow treatment setup employed in this study, the ZVI concentration would last for months before exhaust according to estimates made in previous pilot studies (Huang et al, 2012b). For this study, for example, daily consumption of ZVI was estimated at about 0.6% by weight out of the 900 g ZVI added at the beginning of the test. Therefore, change of ZVI concentration should not be a factor for the duration of the "lag" phase, which leaves the magnetite phase and its characteristics the main factor that contributes to the recovery of the reactivity after the initial disruption for the "lag" phase. The second variable with the hZVI media is the

concentration of the FeOx phase, which upon the completion of media conditioning, the mass of FeOx accounts for about 3% of total solid by weight in the reactor. Once entering continuous-flow treatment, nitrate reduction by the media could result in about an addition of 10 g FeOx in the solid phase per day. Therefore, the FeOx concentration would increase from about 4.5 g/L at day 1 to about 16 g/L at day 7. This is a significant change that may help promote the reactivity of the hZVI media in the first week, which might be a contributing factor to the improved reactivity over time with the high TDS run. However, the increase in FeOx concentration would still not explain fully the behavior of the hZVI during the transition of high TDS influent. The increase in FeOx would similarly help nitrate reduction in all of the controlled runs without high TDS, which was not observed in Run#1. To better explain the improved reactivity during the "lag" phase, we have to look into the potential chemistry processes in the interaction between the FeOx and the anions in the TDS composition. Recent study into the chemistry of FeOx formation and evolution found that the formation of magnetite as the corrosion product by ZVI in the hZVI system is preceded by a precursor that is somewhat close to a greenrust compound. These precursor iron oxide compounds actually incorporate a significant amount of anions such as chloride, sulfate, or even nitrate into a double-layer hydroxide structure. The formation of these precursors plays a key role in nitrate reduction and selenate reduction by the hZVI media. All these common anions would compete for the available sites which may be regulated by an intrinsic equilibrium constant. When the media is exposed to high TDS wastewater, a

new equilibrium has to be established gradually and until then, nitrate reduction would not be recovered.

This phenomenon could also be explained by what was proposed as the type II adsorption by Railsback in Figure 3.6.5. Essentially, the ions could be incorporated into the magnetite as time passes by and may in term negate the high ionic strength inhibition on the system. Further research is required to determine the exact mechanics behind this phenomenon but it is out of the scope of this study.

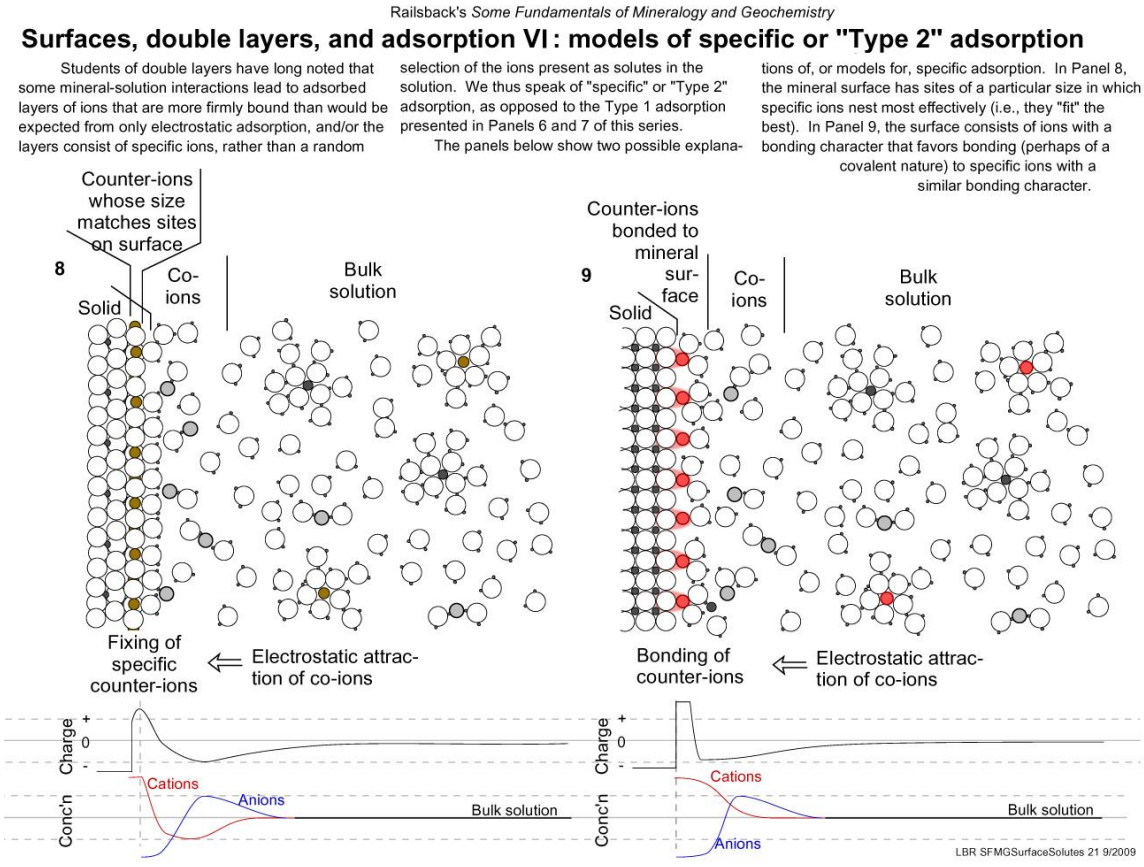


Figure 3.6.5 Type II adsorption mechanism described by L. Bruce Railsback, University of Georgia, providing a possible explanation for the “lag” phase which is characteristic to biological systems to be observed in the pure chemical hZVI system.

Results from these tests help reconcile the contradictory understanding from our previous laboratory and field test results. In a series of batch tests, Huang's group investigate how chloride and sulfate as potential competitive anions would affect selenate reduction in a ZVI/Fe^{2+} reactive system. In these batch tests, ZVI was directly used without converting to hZVI media. Nonetheless, once the reaction started, it was our understanding that magnetite-like iron oxide will start to form as the corrosion product. The test results clearly showed that both chloride and sulfate would exert great hindrance to the reactivity of ZVI media for selenate reduction (Figure 3.6.6). The batch tests last no more than 24 hr with limit presence of Fe3O4 in the end. If results from these batch tests could be extrapolated to hybrid ZVI and FGD wastewater treatment, we would expect that high chloride and sulfate in real FGD wastewater would greatly slow down nitrate and selenate reduction. In multiple field pilot demonstration that involved treating FGD wastewaters of varying strengths and TDS, we found no obvious correlation between TDS and system performance, even though the complicated field test conditions rendered it difficult to draw a definite conclusion on the impact of high TDS. The latest results from this study support our understanding that high TDS indeed has limited impact on hZVI system performance on a long-term operation bases. The previous laboratory batch tests with limited presence of FeOx phase and on a short-term base should not be extrapolated to predict the impact of high TDS or competitive anions on hZVI system performance.

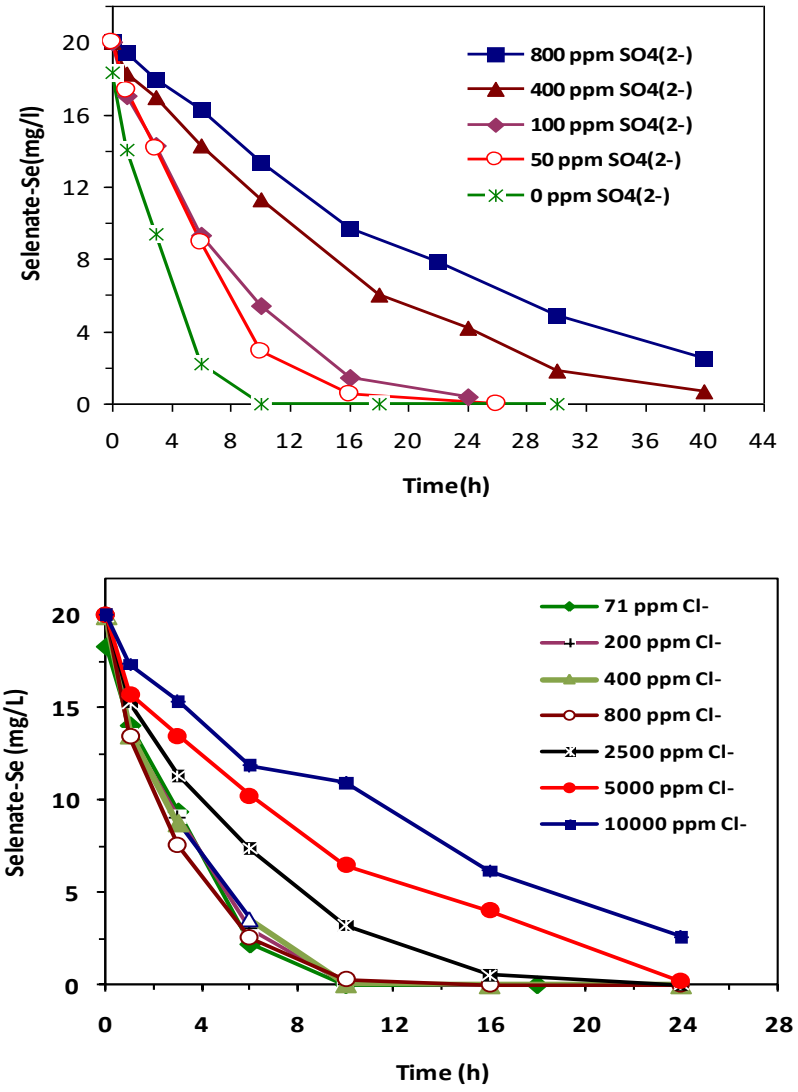


Figure 3.6.6 Selenate reduction over time in 10 mL serum vial reactors with initial conditions controlled as: 0.5 g (or 50 g/L) ZVI + 10 mL liquid with 1.0 mM Fe^{2+} + 20 mg/L selenate-Se and varying concentrations of chloride and sulfate added as NaCl and Na_2SO_4. The results showed the presence of high concentration of Cl^- and SO_4^{2-} could greatly decrease selenate reduction rate in the ZVI/Fe^{2+} reactive system.

Findings from this study improve our understanding of the hZVI and expand its application scopes and flexibility for industrial applications in some of the most challenging wastewater. For the FGD wastewater application, the increasingly concentrated dissolved solids due to increased water recirculation, mainly chlorides, will not affect hZVI system performance. This provides a major advantage to the hZVI technology over other competing technologies such as biological selenium removal processes as the trend towards higher water recirculation cycles continues in the future. Alternatively, the tolerance of high TDS could enable a novel use of the hZVI system in conjunction with membrane technologies for achieving water reuse purpose or ZLD applications. For example, a low strength wastewaters such as mining drainage could be first processed through RO systems; the filtrate could be used as new water resources; while the concentrate could be treated with hZVI to remove heavy metals and discharge. With RO pretreatment, only concentrate with high TDS needs to be treated and thus the hZVI system could be significantly reduced compared with directly treating the low strength wastewater. This approach could greatly reduce the overall costs, both the capital and O&M costs, and still have high quality R/O filtrate as new water resources.

4. IMPACT OF HIGH MANGANESE ON HYBRID ZVI TREATMENT SYSTEM

4.1 Bench-top hZVI Treatment System

The hZVI reactors and the experimental setup were identical to the ones used in previous chapter for studying the impact of high TDS on hZVI performance.

4.2 Materials

All chemicals including ZVI were identical to those described in Chapter 3. Al^{3+} was prepared using aluminum chloride solution (0.5M, Ward's Science, laboratory grade). Mn^{2+} was prepared using manganese chloride tetrahydrate (VWR, ACS grade).

4.3 Sampling and Analysis

The sampling procedure and relevant analytical methods for Fe^{2+}, nitrate analyses were described in Chapter 3. Dissolved Mn in water was analyzed using either an IC method or an AAS method, both reporting a detection limit of about 0.1 mg/L.

4.4 Experimental Design and Rationale

Low concentration of Mn^{2+}, e.g. at < 5 mg/L, is common in FGD wastewater, which could be removed effectively by hZVI and had little impact on the system performance for long term operation according to field pilot tests (Huang et al. 2012) . High concentration of Mn^{2+}, however, had been observed to interfere with hZVI performance. With physical chemical properties similar to those of Fe(II) in many aspects, Mn(II) could be incorporated into the iron oxides of the hZVI media.

Preliminary tests showed that FeOx incorporated with a large amount of Mn(II) was tinted with a brownish color compared to black color of the typical hZVI media.

The objective of this experimental study is to evaluate effects of high concentration of dissolved Mn^{2+} in the wastewater on the hZVI system in two aspects: how high Mn^{2+} could affect hZVI reactivity on a long term operation; and if hZVI system could consistently remove high Mn^{2+} with high efficiency. Our approach is similar: operating bench-top hZVI systems to continuously treat simulated wastewater on a long term base to evaluate potential factors/conditions that may promote Mn^{2+} removal and maintain high reactivity of hZVI media in presence of high Mn^{2+}. First trial run is to supply trivalent metal ion and sodium hydroxide to the system that may promote the formation of green rust. If Mn^{2+} could be immobilized and incorporated into the green rust, its interference with the hZVI system might be eliminated. One study also reported that manganese, in the presence of hydroxides, could promote magnetite formation from green rust (Inoue et al, 2007), which would be beneficial to the hZVI system. Trivalent aluminum was chosen as the trivalent metal ion for this study as it was previously shown that Al^{3+} does not adversely impact ZVI reactivity (Huang et al, 2003). The second approach proposed to mitigate the negative effects of high Mn^{2+} was to raise the magnetite mass ratio in the hZVI media before exposing the media to Mn^{2+}. With an abundant supply of magnetite already in the media system, Mn concentration in the FeOx phase could be diluted and remained low, thus minimizing its potential impact on the chemical properties of the FeOx phase. Lastly, aeration treatment was also studied for its interaction with the hZVI system with the presence of manganese. Aeration is a

common technique used in the water treatment industry to precipitate some common metal ions such as iron and manganese (Aziz et al, 1992). Since dissolved iron is the cornerstone in the hZVI system, aeration should have a significant impact in this condition as both manganese and iron are present in the dissolved form. Again, nitrate was used as the performance indicator of the hZVI media on top of monitoring the manganese removal levels.

4.5 Operation and Control of the hZVI Treatment System

Similar to previously established methods, this test started with 300 g of 325 mesh ZVI added to the reactors for a concentration of 50 g/L and doped with 10mM nitrate and 7mM ferrous iron to precondition for 24 hours before the influents were fed. The performance indicator, nitrate, was spiked in the influent at a level of 1.5mM (21mg/L) along with 1mM (54mg/L) of Mn^{2+}. The reagent feed consisted of Fe^{2+} and Al^{3+} at concentrations of 2.0 mM and 1.0 mM, respectively. Sodium hydroxide was also fed as a reagent at a dosage of 1.0 mM, 3.0 mM, and 5.0 mM starting on Day 1, Day 4 and Day 18, respectively. A second hZVI system was operated in parallel as a control under same conditions except that no Al^{3+} and NaOH reagents were added.

The 1st Run last not long due the low initial ZVI concentration. A 2nd Run was conducted with a higher initial ZVI concentration. For the 2nd Run, 900 g of 325 mesh ZVI was added to the reactors, corresponding to a concentration of 150 g/L. The reactor was then doped with nitrate at 20 mM and Fe^{2+} at 14 mM and operated as a batch reactor to precondition the media for 24 hours. The performance indicator, nitrate, was spiked in

the influent at a level of 1.5 mM (21 mg/L) alone with 0.5 mM (27 mg/L) of Mn^{2+}. The manganese level was reduced to decrease Mn load on the media. The reagent feed consisted of Fe^{2+} and Al^{3+}, both at a dosage of 1.0 mM. NaOH solution was fed at a dosage of 1.0 mM, but was stopped on Day 6.

Run#3 was conducted to evaluate high initial FeOx mass as a potential solution to reduce Mn impact on the media reactivity. For the purpose, the ZVI media in the reactor was first processed using the preconditioning method for an extended period that resulted in 50% of the ZVI (i.e., 450 g) being converted to magnetite. Based on the reaction equation of nitrate reduction by ZVI/Fe^{2+} (Huang et al. 2003), a total of 450 mM of nitrate and 315 mM of Fe^{2+} (note: the quantity is based on 6 L reactive volume) was dosed into the hZVI reactor at the rate of 30 mM and 21mM per day, respectively, for 15 days. Residual nitrate concentration was monitored before the next dose was added. Residual nitrate never exceeded 1 mg/L during the preconditioning process. Treatment test started only after 15 days of preconditioning with a high concentration of FeOx (est. at >100 g/L) in the media. The influent feed consisted of nitrate at 1.5 mM (21 mg/L) as the hZVI system performance indicator and 0.5 mM (27 mg/L) Mn^{2+}. The reagent feed consisted of Fe^{2+} at a dosage of 1.0 mM.

Run#4, the last test, was conducted to evaluate aeration as a potential tool for dealing with high Mn2+ in the hZVI system. Like the previous tests, 900 g of 325 mesh ZVI was added to the reactors for a concentration of 150 g/L and doped with 20mM nitrate and 14mM ferrous iron to precondition for 24 hours before the influents were fed. The performance indicator, nitrate, was spiked in the influent at a level of 1.5 mM (21

mg/L) along with 0.5 mM (27 mg/L) of Mn^{2+}. The reagent feed consisted of Fe2+ at a dosage of 1.0 mM. Aeration was provided using an aeration pump at a rate of 1.0 L/min. Air bubbles were discharged at the bottom of the reaction zone. During the first three days, no Mn^{2+} was spiked in the influent to establish a baseline level of nitrate in the aerated hZVI system.

4.6 Results and Discussions

Impact of NaOH

Compared to the baseline reactor, the reactor operated with added Al^{3+} and NaOH did have a higher nitrate removal rate, at least until roughly the 10^{th} day. This performance was not sustained past the 15^{th} day, after which the reactor fed with Al^{3+} and NaOH performed slightly worse than the control system, see figure 4.6.1. When judging the hZVI system's reactivity using nitrate, it is clear that both reactors had a deterioration of performance as time passes, but the reactor with Al^{3+} and NaOH feeds experienced a sharper performance decrease. The addition of Al^{3+} and NaOH essentially traded long-term performance for a temporary boost, which is less than ideal in the context of wastewater treatment, but potentially useful in an emergency situation for dealing with a sudden spike of high manganese in influent wastewater. No significant Mn^{2+} removal was achieved by either of the reactors, as shown in figure 4.6.2. This suggests that adding Al^{3+} and NaOH have no significant effect on Mn^{2+} removal. The hypothesis of green rust formation from the interaction of Al^{3+}, Mn^{2+} and NaOH with the hZVI media as a viable solution for removing Mn^{2+} was not validated.

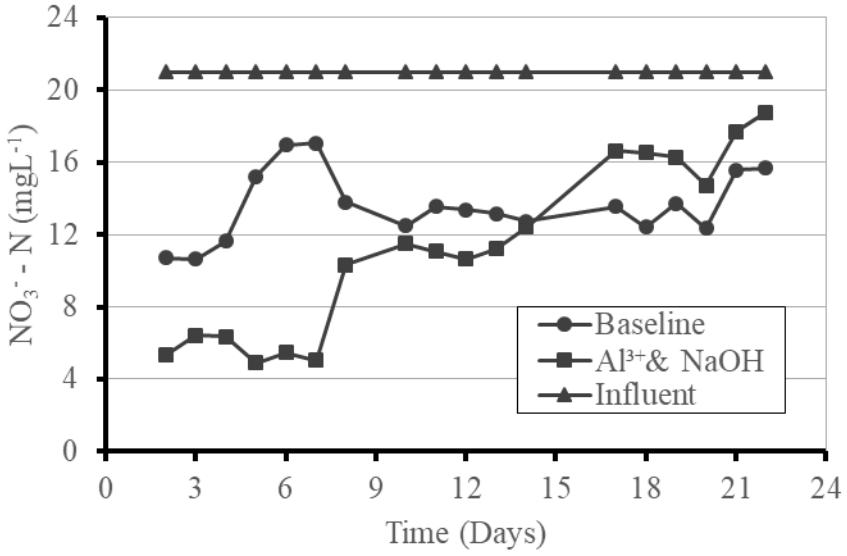


Figure 4.6.1 Nitrate reduction over time in Run#1. Reactors started with 50 g/L ZVI. The addition of Al^{3+} and NaOH appeared not helpful for maintaining high reactivity of hZVI media when exposed to high Mn^{2+} in a long term operation.

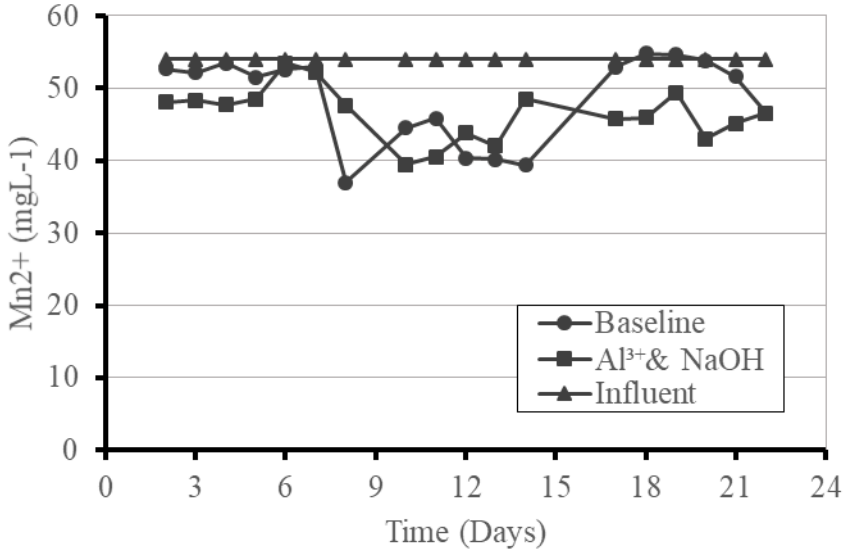


Figure 4.6.2 Removal of dissolved Mn^{2+} over time in Run#1. The addition of Al^{3+} and NaOH into the hZVI system did not help Mn^{2+} removal.

The second test (Run#2) was conducted with three times as much ZVI initially. Mn^{2+} loading was also lowered by half since reactors in Run#1 lost reactivity rather quickly. The hydroxide feed was stopped at Day 6 as it appeared to worsen nitrate and manganese removal performance, while Al^{3+} feed was maintained. Overall, there was virtually no difference in the nitrate removal rates before or after the hydroxide feed was stopped, as seen in Figure 4.6.3. In contrast to the previous test, nitrate removal increased to around 65% toward the end of the test duration. Although nitrate removal is significantly better than that observed in Run#1, it is still far from the 95%+ efficiency that a similar system could achieve in the absence of high Mn^{2+} in the influent. In terms of manganese removal, reactor fed with Al^{3+} has worse performance consistently after the first few days, as in Figure 4.6.4, which is consistent with Run#1 results.

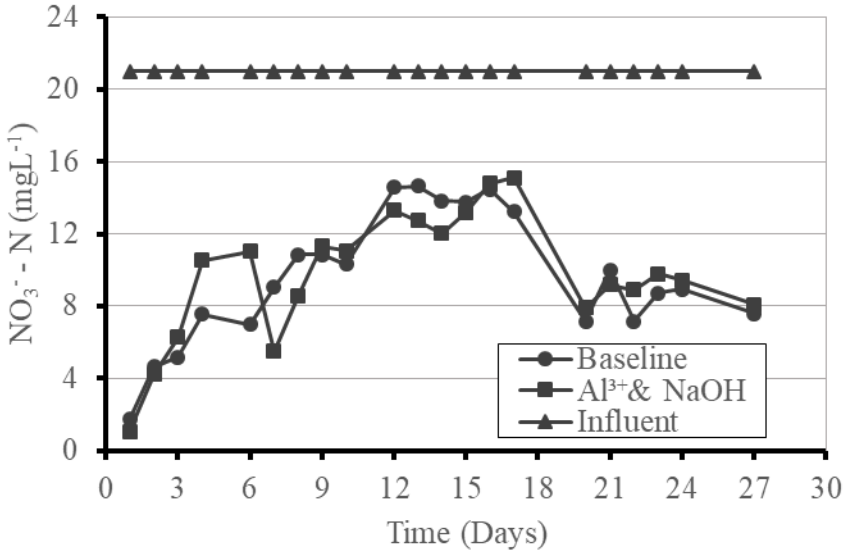


Figure 4.6.3 Nitrate reduction over time in Run#2. Reactors started with 150 g/L ZVI. The addition of Al^{3+} and NaOH appeared not helpful for maintaining high reactivity of hZVI media when exposed to high Mn^{2+} in a long term operation.

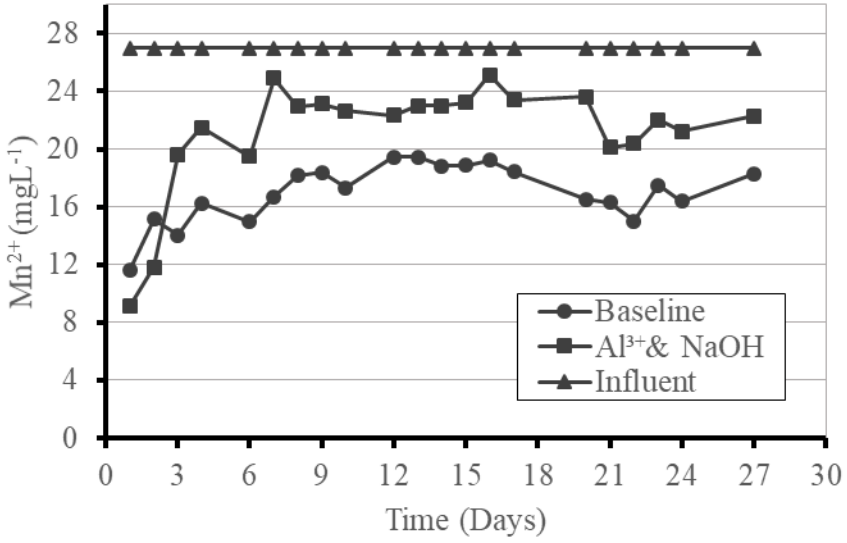


Figure 4.6.4 Mn^{2+} removal over time in Run#2. Reactors started with 150 g/L ZVI. Mn^{2+} in the influent was lowered to 27 mg/L. Even with decreased Mn^{2+} dosage in the influent, the hZVI system could not remove Mn^{2+} effectively, with or without adding Al^{3}+. In fact, Al^{3+} appeared to further hinder Mn^{2+} removal.

Impact of High Magnetite Concentration on Mn Removal

The high magnetite reactor performance was compared to the baseline reactors from the previous tests in this series for analysis. Prior to day 16, higher initial magnetite did provide better nitrate removal rate compared to its low magnetite counterpart as predicted, see figure 4.6.5. However, after day 16, the performance drops significantly without signs of recovery. Higher magnetite did not achieve the desired effect of overcoming the long-term negative impacts of manganese as intended. Surprisingly, the best combination for nitrate removal was ZVI concentration at 150g/L and a small initial amount of magnetite. This could be due to the flexibility and higher reservoir of electrons from a larger amount of ZVI, or possibly more surface on the ZVI media that was not covered by magnetite. Through the complex iron and green rust chemistry, it is possible that manganese eventually incorporated into the hZVI media surface and formed relatively compatible types of iron-manganese oxides which was possible only when sufficient unspent ZVI was available in the system. Looking at figure 4.6.6, we can see that initially, the high magnetite reactor had worse manganese removal capacity but quickly levels off with the baseline reactor. It would appear that higher amount of magnetite had no significant impact on manganese removal on the long term. Higher magnetite reactor even have worse manganese removal performance after 21 days, suggesting that more developed magnetite has less compatibility with manganese in the system than its lower magnetite counterpart. The higher performance observed initially could be attributed to higher sorption capacity created simply by having large amounts of magnetite present in the system.

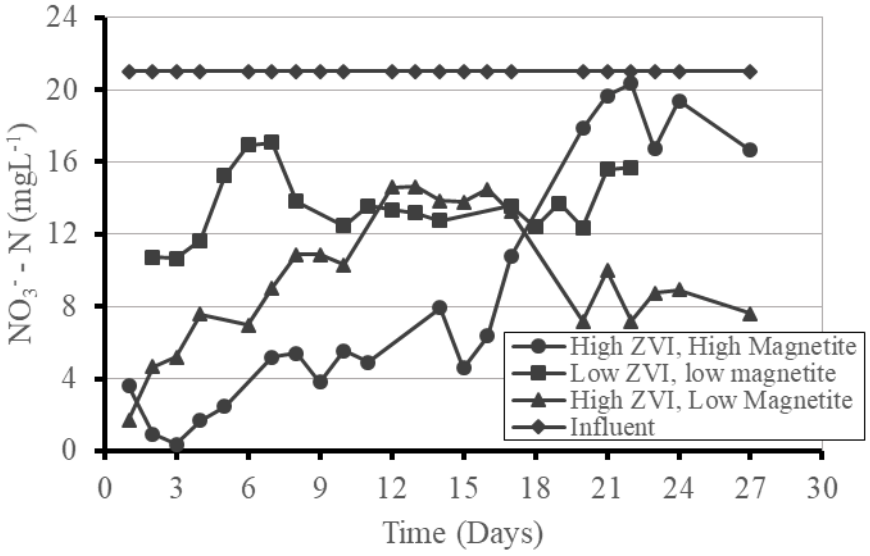


Figure 4.6.5 Nitrate reduction over time in Run#3. Run#3 started with a hZVI media produced from extended preconditioning process that converted 50% of ZVI (450 g) into magnetite (~700 g) before continuous flow treatment started. High initial magnetite concentration appeared help mitigate negative impact of Mn^{2+} on the media reactivity with respect to nitrate reduction. But the system still gradually loses reactivity on the long run.

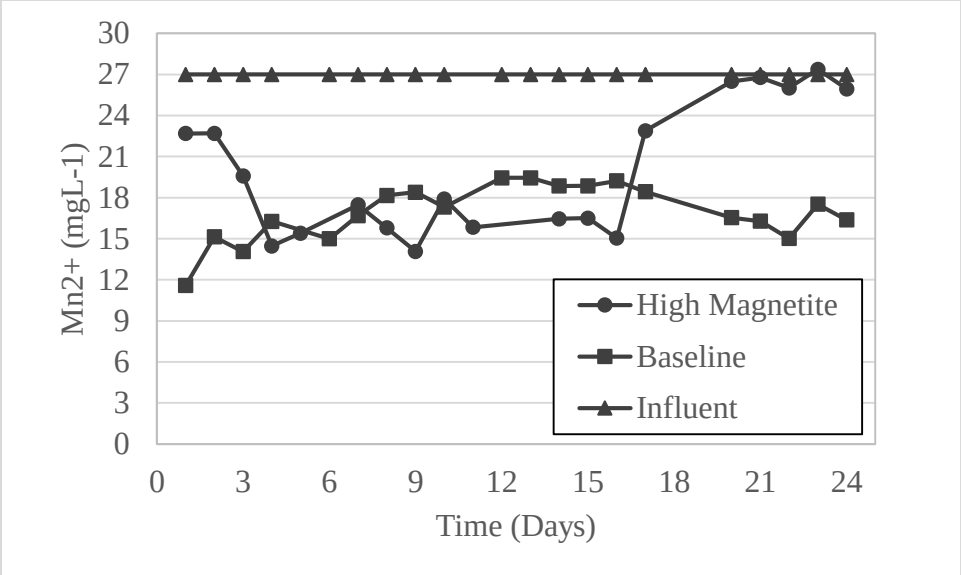


Figure 4.6.6 Residual manganese levels of high magnetite reactor compared to baseline preconditioning, higher amounts of magnetite did not improve manganese removal rates in the hZVI system

Effect of Aeration on hZVI and Mn^{2+} removal

Applying aeration in the hZVI system (Run#4) had produced excellent results with respect to nitrate removal, which is as good as the system treating a comparable wastewater but without the additional manganese, as seen in Figure 4.6.7. After Day 15, the reactor experienced a sudden decrease of nitrate removal performance, and essentially crashed thereafter. Mn concentration in the treated effluent steadily rose during the test course (Figure 4.6.8), but nitrate removal was not affected. Virtually neither nitrate nor manganese was removed after Day 21. The rapid collapse of the hZVI system was most likely due to the exhaust of ZVI in the reactor. It has been proven that hZVI could rapidly react with O_2 in the air. At an aeration rate of 1 L per minute, about

12 mol (or 384 g) of O_2 was introduced into the reactor per day, which was adequate to consume more than 900 g of ZVI. Although the usage rate of O_2 by the reactor media during the aeration is not known, it is conceivable that most ZVI had been consumed after 15 days aeration. Therefore, aeration is capable of promoting hZVI reactivity for nitrate reduction. The role of aeration in promoting Mn^{2+} removal was not clear.

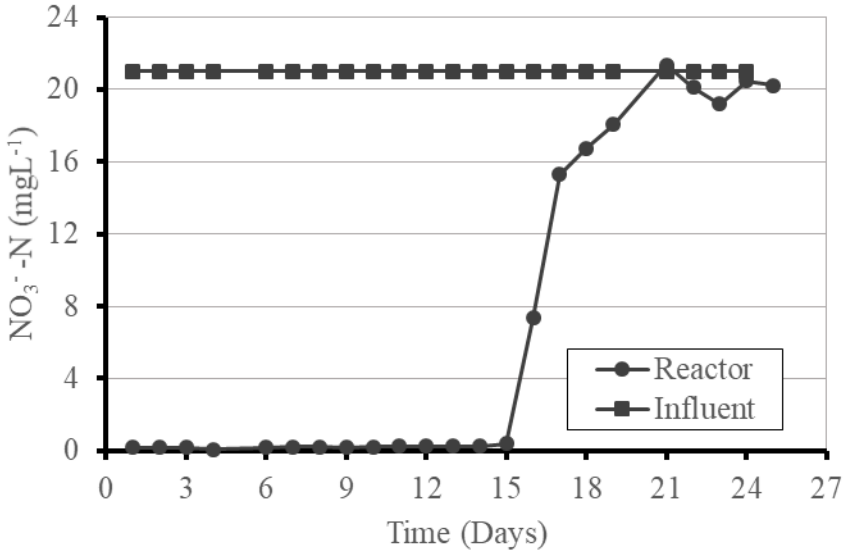


Figure 4.6.7 Nitrate removal over time in Run#4 with the introduction of aeration in the hZVI system. Aeration appears to greatly promote nitrate reduction by the hZVI mediea in the presence of Mn^{2+}. The system's reactivity quickly collaped after Day 15, likely due to rapid consumption of ZVI material by the aeration process.

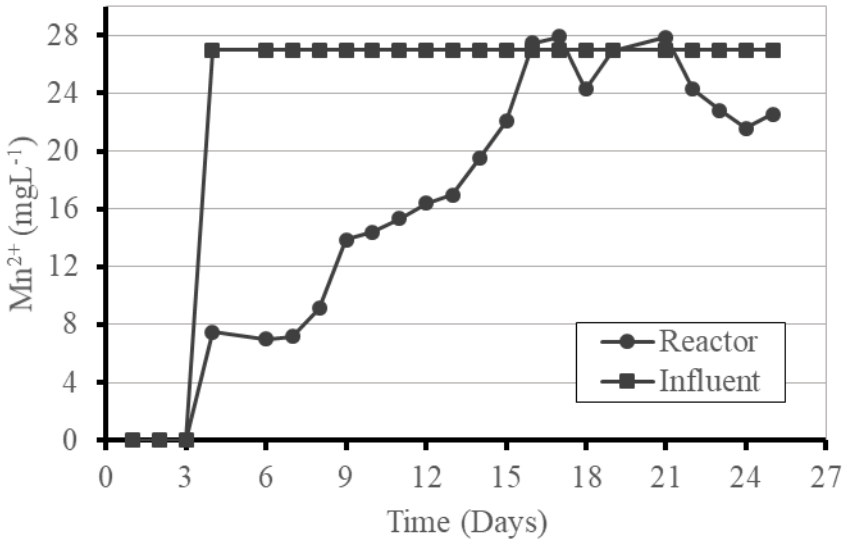


Figure 4.6.8 Mn^{2+} removal over time in Run#4 with the appliation of aeration in the hZVI system. Dissolved Mn^{2+} in the treated effluent slowly creeped up. The time manganese was no longer removed in the reactor coincided with the time where nitrate removal capacity suddenly dropped

Discussion

From the tests conducted in this study, it is clear that manganese, at levels of 0.5 mM or 27 mg/L could produce significant hindrance for FGD water treatment by hZVI system with respect to nitrate reduction. Fortunately, impact of high Mn^{2+} on hZVI reactivity for selenium and mercury removal appears to be limited based on other laboratory and field test results. The potential constrain from a high Mn^{2+} wastewater may not pertain to all FGD wastewater applications as FGD water tends to have very site specific characteristics. Manganese levels have been reported to be as high as 225 mg/L in Homer City and as low as 2.78 mg/L in Widow's creek (EPA, 2009). With a variation

like this it is hard to administer a single solution against manganese for the hZVI system application. Although these tests failed to identify a method to directly counteract the negative impacts of manganese within the hZVI system itself, it did recognize that manganese should be a part of consideration when designing and implementing this technology in FGD water applications. What could be done in sites like Homer City, where the manganese levels are really high, is to pretreat the waste stream targeting manganese. The pretreatment could enable hZVI system to perform at optimal conditions where it can target other contaminants more effectively such as mercury, arsenic, and selenium, among others.

5. IMPACT OF HIGH NICKEL ON HYBRID ZVI TREATMENT SYSTEM

5.1 Bench-Top hZVI Treatment System

The hZVI reactors and the experimental setup were identical to the ones used in previous chapter for studying the impact of high TDS on hZVI performance.

5.2 Materials

All chemicals including ZVI were identical to those described in Chapter 3. Ni^{2+} was prepared using nickel chloride hexahydrate (Alfa Aesar, > 98% purity).

5.3 Sampling and Analysis

The sampling procedure and relevant analytical methods for Fe^{2+} and nitrate analyses were described in Chapter 3. Dissolved Ni in water was analyzed using either an IC method or an AAS method, both reporting a detection limit of about 0.1 mg/L.

5.4 Experimental Design and Rationale

Nickel is also often present in FGD wastewater, but typically at a lower concentration than manganese. High Ni^{2+} is often found in electroplating wastewater, often reporting hundreds of milligram per liter. Due to its similarity with iron and manganese, Ni was chosen as a target metal for examining the hZVI system capacity for handling extremely high-strength waste stream like the FGD wastewater or electroplating wastewater. Experiments in this study were designed with aims to evaluate how high Ni^{2+} would affect the hZVI system performance with nitrate

reduction, and to explore methods and operation conditions that may help hZVI achieve high Ni^{2+} removal rate. For the purpose and based on our understanding of the hZVI chemistry, three variables, namely dissolved Fe^{2+}, nitrate dosage, and aeration, were selected to evaluate for their impact on the interaction between the hZVI media and Ni^{2+}. In Run#1, by operating one hZVI system with and the other without adding Fe^{2+}, we aimed to examine whether Fe^{2+} will facilitate or impede the removal of Ni^{2+} in the hZVI system. Nitrate is widely present in both FGD wastewater and electroplating wastewater, and also is the oxididant we often use in media conditioning process for reacting with ZVI to form magnetite as the corrosion production. In Run#2, with nitrate as the controlled variable, we aim to understand if nitrate-induced iron corrosion/magnetite formation chemistry could help or impede Ni^{2+} removal. It was well understood that the co-presence of Fe^{2+} and nitrate in a ZVI system could promote nitrate reduction, accompanied with the consumption of Fe^{2+} by hZVI media. Whether or not a similar relationship exists between Ni^{2+} and nitrate is an intriguing question that deserves investigation. Finally, aeration was applied in the reaction zone of the hZVI system, which could greatly accelerate ZVI corrosion, forming great amount of magnetite or other iron oxides depending on the chemical condition, which in turn may greatly affect the fate and transformation of Ni^{2+} in the hZVI system.

5.5 Operation and Control of the hZVI Treatment System

All three runs in this study were started with new hZVI media preconditioning process as described in Chapter 3. For Run#1, the simulated wastewater influent was

spiked with 100 mg/L Ni^{2+} but later reduced to 20 mg/L at Day 9. The reagent feed consisted of 1.0 mM of Fe^{2+}, which was kept constant throughout the test. The second reactor was set up as the control and operated similarly except that no Fe^{2+} was added into the system. For Run#2, the wastewater influent was spiked with 100 mg/L Ni^{2+} and 1.5 mM (21mg/L) nitrate, the latter of which was doubled to 3.0 mM (42 mg/L) on Day 7. The reagent feed consisted of 1.0 mM Fe^{2+}. The second hZVI system was again set up as the control and operated similarly except that no Fe^{2+} was added into the system. For Run#3, the influent was also spiked with 100 mg/L Ni^{2+}, and no reagent feed was used. Aeration was introduced at a rate of 1.0 L/min near the bottom of the reaction zone. The air flow was controlled and monitored using an air flow gage. A small aquarium air pump purchased from local Walmart store was used. Similarly, a separate hZVI treatment system was set up and operated similarly but without being aerated.

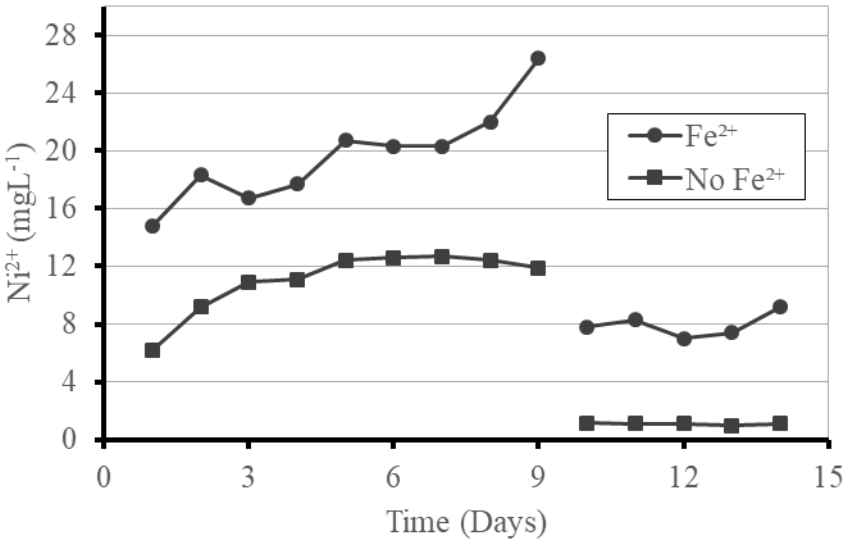
5.6 Test Results and Discussions

Impact of Externally-Added Fe^{2+}

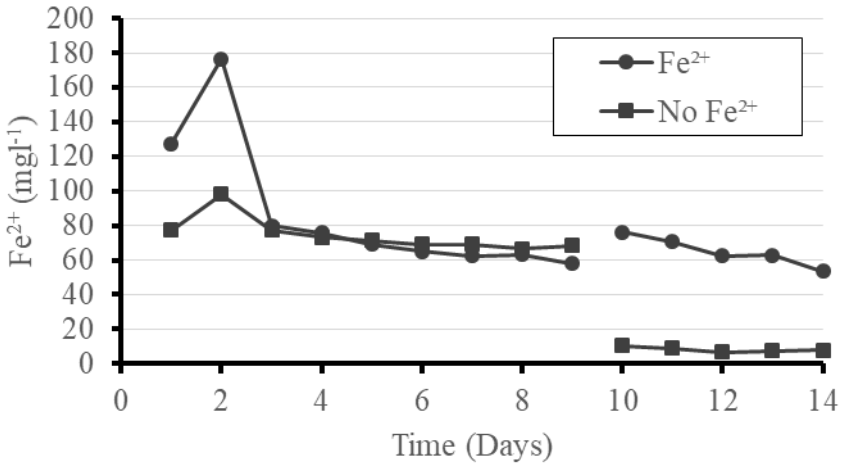
As shown in Figure 5.6.1, the hZVI system without feeding Fe^{2+} achieved about 90% removal of dissolved Ni^{2+} for both dosages of 100 mg/L and 20 mg/L Ni^{2+} in the wastewater influent. When 1.0 mM Fe^{2+} was dosed into the hZVI system, Ni^{2+} removal decreased in the hZVI system, with Ni^{2+} increased by about 10 mg/L in the treated effluent for both 100 and 20 mg/L Ni^{2+} influent. Noticeably, even in the test without adding Fe^{2+}, dissolved Fe^{2+} was found in the reactor. In the test with 100 mg/L Ni^{2+} in

the feed, the decrease of 90 mg/L (1.53 mM) Ni^{2+} corresponds to a release of about 70 mg/L (1.25 mM) of Fe^{2+}; In the test with 20 mg/L Ni^{2+}, the removal of 18 mg/L (0.30 mM) Ni^{2+} corresponds to a release of about 8 mg/L (0.1 mM) Fe^{2+}. Ni^{2+} is likely directly responsible for releasing dissolved Fe^{2+} from the hZVI media, possibly through a cation substitution mechanism to replace Fe(II) in the FeOx structure, which could be represent as $Ni^{2+} + Fe^{(II)}Fe^{(III)}O_X \rightarrow Fe^{2+} + Ni^{(II)}Fe^{(III)}O_X$. This substitution reaction may help explain a rather stable ratio of dissolved Ni^{2+}/Fe^{2+} observed in Run#1: e.g., in the test with 100 mg/L Ni^{2+} without augmenting Fe^{2+}, it was roughly 70 mg/L Fe^{2+} vs. 10 mg/L Ni^{2+}, which later changed to about 8 mg/L Fe^{2+} vs. 1.2 mg/L Ni^{2+}. In the tests with adding 1.0 mM Fe^{2+}, it was roughly 60 mg/L Fe^{2+} vs. 8 mg/L Ni^{2+} for the test period of 20 mg/L Ni^{2+} in the feed. These results suggested a likely equilibrium ratio of about 7 to 1 in molar ratio between dissolved Fe^{2+} and Ni^{2+} when interacted with the hZVI media. The test period of 100 mg/L Ni^{2+} with additional 1.0 Fe^{2+} appeared to have a certain disruption or abnormity after Day 3 in term of dissolved Fe^{2+} concentration. The 7:1 ratio of Fe^{2+}/Ni^{2+} upon equilibrium suggests that Ni^{2+} is the preferred ion when hZVI takes in metal ions. Results from Run#1 are quite different from the behaviors observed in the interaction between Mn and the hZVI media from the earlier tests (see chapter 4). In the hZVI media system, Ni^{2+} could play a role similar to Fe^{2+}, and thus could substitute Fe^{2+} to some degree and share the fate similar to Fe^{2+} with relationship with the hZVI media. It could not be excluded that a cation substitution equilibrium between Fe^{2+} and Mn^{2+} in the hZVI media system may also exist, but the ratio of Fe^{2+}/Mn^{2+} could be much smaller than 7 to 1 observed for the

Fe^{2+}/Ni^{2+}, therefore, the hZVI media would prefer taking in Fe^{2+} over Mn^{2+} when there is a chance.



(a)



(b)

Figure 5.6.1 Time courses of dissolved Ni^{2+} (Panel a) and Fe^{2+} (Panel b) in the effluent of the two hZVI systems from Run#1: one system fed with 1.0 mM Fe^{2+}, the other without adding Fe^{2+} reagent. In the absence of externally added Fe^{2+}, the hZVI system achieved about 90% nickel removal for treating both dosages of 100 mg/L and 20 mg/L Ni^{2+} in the influent. Adding Fe^{2+} decrease Ni^{2+} removal.

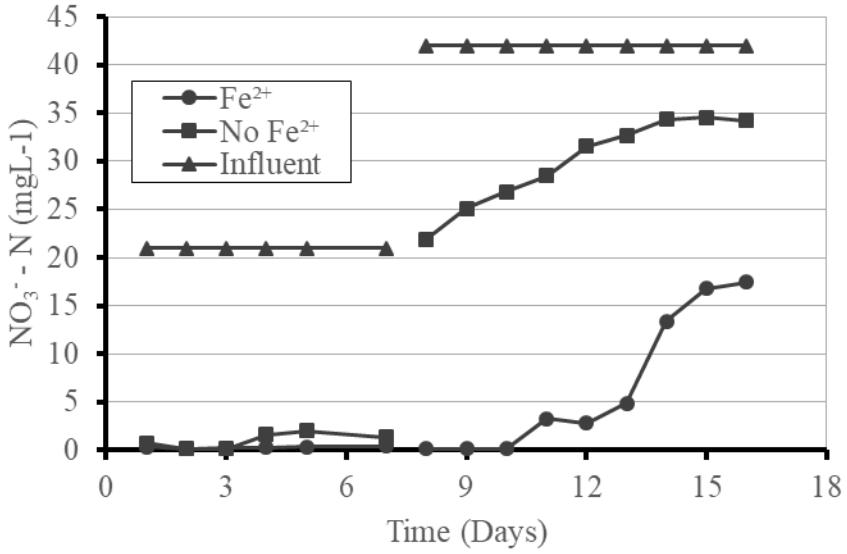
Impact of Nitrate

Nitrate, as explained previously, can be used to gage the reactivity of an hZVI system in operation. Several interesting phenomena were observed when nitrate was added in the influent along with Ni^{2+}. The Ni^{2+} dosage for Run#2 was 100 mg/L, same as Run#1. With the addition of 21 mg/L (1.5 mM) nitrate-N, both hZVI treatment systems with or without adding Fe^{2+} saw an increase in nickel removal (Figure 5.6.2). In the test with addition of 1.0 mM Fe^{2+} as reagent, a decrease of Ni removal at about 10 mg/L was observed again as in the test with Fe^{2+} in Run#1, confirming the mutual competitive nature of Fe^{2+} and Ni^{2+}. Nitrate removal during the first week was excellent in both hZVI systems with or without adding Fe^{2+}, decreasing nitrate from 21 mg/L in the influent to below 0.5 mg/L in the effluent with a removal efficiency of > 95%.

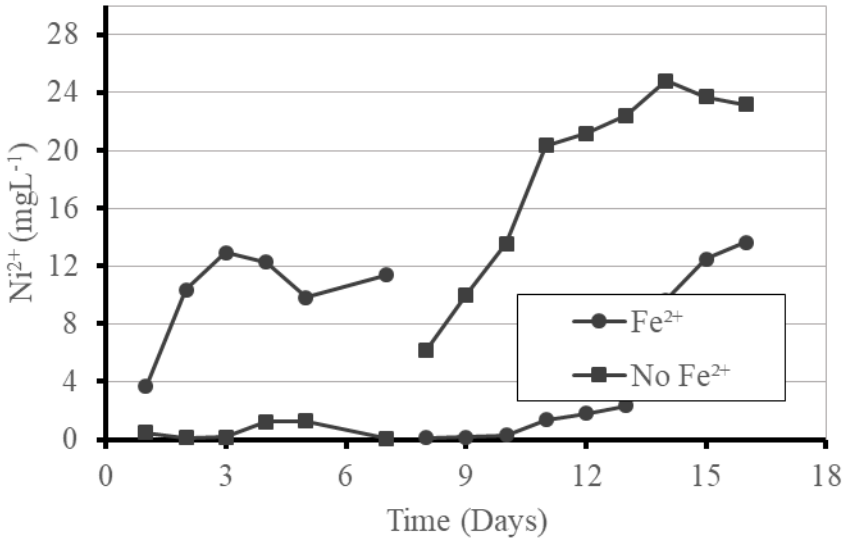
After nitrate concentration in the feed was doubled to 42 mg/L (3 mM) on Day 8, the results were inverted for the two reactors. The hZVI system without augmenting Fe^{2+} saw suddenly drops in both nitrate reduction and Ni^{2+} removal with increased nitrate dosage in the influent. It was understood that 3.0 mM nitrate reduction would require about 2.2 mM dissolved Fe^{2+}. Therefore, 100 mg/L (1.7 mM) Ni^{2+} in the feed would support the complete reduction of nitrate at 1.5 mM but not at 3.0 mM. This could

complicate chemistry in the hZVI and affect the hZVI media reactivity. It is also possible that the continued removal of Ni2+ and its buildup in FeOx phase just crossed the threshold that would start to alter the chemistry and reactivity of FeOx on Day 9. For the test with addition of 1.0 mM Fe^{2+}, increase of nitrate dose to 3.0 mM appeared not immediately affect Ni^{2+} removal, but over time, Ni^{2+} removal still decreased gradually, suggesting that continued buildup of large quantity of Ni in the FeOx would gradually affect the hZVI media's reactivity with respect to nitrate reduction.

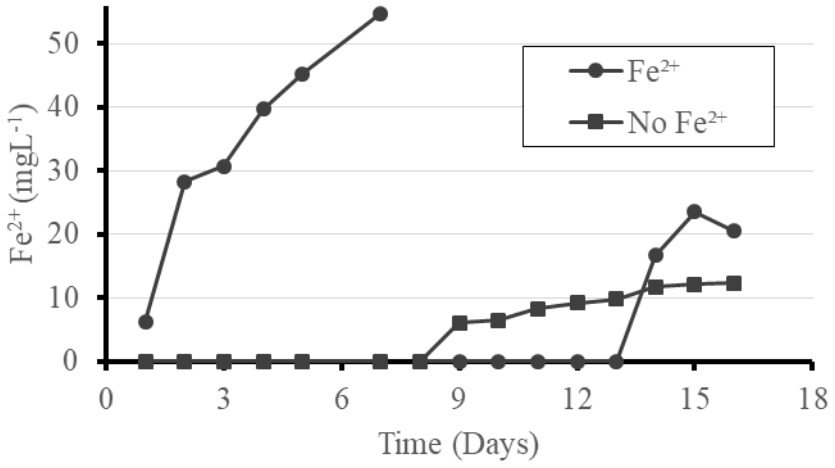
Overall, it could be inferred that the presence of nitrate in the influent and its reduction in the hZVI system would promote Ni^{2+} removal through the production of FeOx. Under a right dosage, it is possible to achieve deep Ni^{2+} removal from 100 mg/L to below 1 mg/L. However, it appears that there might be a limit for Ni mass ratio in FeOx, and when that threshold is crossed, the hZVI reactivity could decrease significantly for both nitrate reduction and Ni^{2+} removal. More studies may be needed in the future to establish an optimal control scheme to operate the hZVI system for achieving high Ni removal in a sustainable and consistent manner.


45
40
35
30
25
20
15
10
5
0
0
3
6
9
12
15
18
Fe2+
No Fe2+
Influent
NO3- - N (mgL-1)
Time (Days)

(a)


28
24
20
16
12
8
4
0
0
3
6
9
12
15
18
Fe2+
No Fe2+
Ni2+ (mgL-1)
Time (Days)

(b)



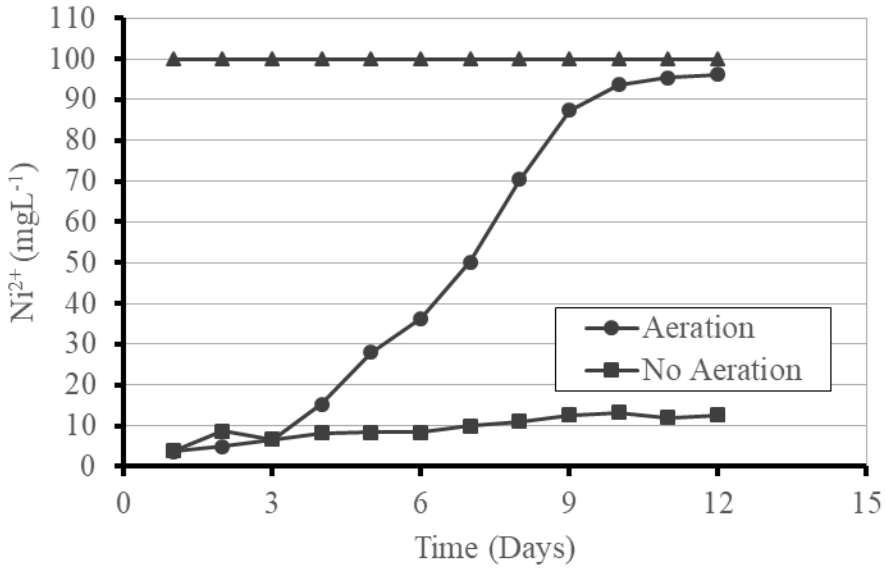
(c)

Figure 5.6.2 Time courses of nitrate reduction (Panel a), dissolved Ni^{2+} removal (Panel b) and dissolved Fe^{2+} (Panel c) observed in the two hZVI treatment systms in Run#2: one system augmented with 1.0 mM Fe^{2+} reagent; the other without feeding Fe^{2+}. The influent contained 100 mg/L Ni^{2+} and 21 mg/L nitrate-N. On day 7, nitrate increased to 42 mg/L as N. The test suggested that with the right dosage of nitrate and Fe^{2+}, it is possible to achieve excellent Ni^{2+} removal so long as Ni buildup in the FeOx phase could be controlled under certain threshold.

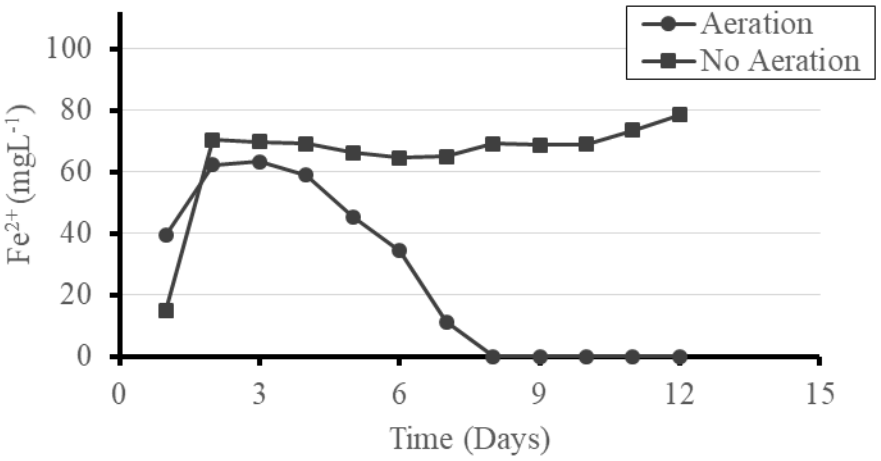
Impact of Forced Aeration

In Run#3, Ni^{2+} removal was evaluated with or without forced aeration in the hZVI reactor. The aerated reactor steadily lost nickel removal capacity while the non-aerated reactor was much steadier with respect to Ni^{2+} removal (Figure 5.6.3). This could also be due to the fact that under intense aeration, the iron oxides formed in the reactor were not magnetite that is essential in supporting high reactivity of the hZVI system.

This is reminiscent to early adoptions of ZVI technology where the surface of ZVI quickly loses reactivity as it reduces contaminants. As mentioned earlier, magnetite is formed in an iron chemistry pathway that typically features a slow to moderate oxidation rate. High intensive aeration exposes the hZVI media to oxygen, which is a strong oxidant that tends to form ferric oxides such as lepidocrocite (γ-FeOOH) or maghemite (γ-Fe_2O_3) from either ZVI corrosion or the oxidative precipitation of dissolved Fe^{2+}. In fact, the color of the aerated reactor changed drastically as the test went on. The solid media resembles a red, brownish color rather than the pure black that is observed in the non-aerated reactor with hZVI media, further proving the intensive aeration had altered the iron oxide compositions and destroy the basic property that enable the high reactivity of a hZVI media system.


110
100
90
80
70
60
50
40
30
20
10
0
0
3
6
9
12
15
Ni2+ (mgL-1)
Time (Days)
Aeration
No Aeration

(a)


100
80
60
40
20
0
0
3
6
9
12
15
Fe2+ (mgL-1)
Time (Days)
Aeration
No Aeration

(b)

Figure 5.6.3 Time courses of dissolved Ni^{2+} removal (Panel a) and dissolved Fe^{2+} (Panel b) observed in the two hZVI treatment systms in Run#3: one system was operated normally; the other with aeration at 1.0 L/min. The results showed that aeration will not help Ni^{2+} removal by the hZVI system.

Discussion

The three hZVI test runs with nickel shed some light on the interaction of Fe^{2+} and Ni^{2+} in the hZVI system. From the test results, it could be inferred that dissolved Ni^{2+} may behave similarly to Fe^{2+} and shared a similar role and fate of Fe2+ in the hZVI system. The presence of nitrate and its removal by the hZVI system could trigger a complicated dynamic among FeOx formation, competitive uptakes of Fe^{2+} vs. Ni^{2+} by hZVI, and the buildup of Ni^{2+} in the FeOx phase. Although such a dynamic is still not fully understood, it appears that it is possible to operate the hZVI system with the right dosage of nitrate and Fe^{2+} for achieving a sustained deep reduction of Ni^{2+} from a wastewater stream contaminated with extremely high Ni^{2+}. The results suggested that hZVI could be used directly to treat electroplating wastewater featuring high Ni2+ and a pretreatment to decrease Ni^{2+} is not a must. Ni^{2+} is a more challenging pollutant than Mn^{2+} as Ni^{2+} could not be easily removed like Mn^{2+} through aeration or chemical oxidation (Horikawa et al, 2000).

The mechanism behind Ni^{2+} removal by the hZVI media is still not very clear, but generally the test results point towards two potential mechanisms: First, Ni^{2+} could be removed through cation substitution when Ni^{2+} interact with FeOx with mixed Fe(II)

and Fe(III) as in the magnetite of the hZVI media. Second, Ni^{2+} could be reduced by ZVI through redox reaction, which resulted in the formation of Ni^0 and the oxidation of Fe^0 to Fe(II). The two pathways may both contribute to Ni^{2+} removal under different aquatic and media conditions. More in-depth study is needed in the future.

6. SUMMARY

The hybrid zero-valent iron (hZVI) technology is a novel chemical treatment platform capable of removing a broad spectrum of heavy metals from a contaminated wastewater in compliance with many of the most stringent wastewater. In this study, we investigate how exceptionally high concentrations of total dissolved solids (TDS), Mn^{2+} and Ni^{2+} in some wastewaters could affect the hZVI media reactivity and system performance. For the purpose, bench-top hZVI treatment system were operated to treat synthetic wastewater with designed composition under controlled conditions. The results showed that TDS as high as 62 g/L, with 35 g/L of Cl^- and 3 g/L of sulfate, may temporarily decrease the hZVI media reactivity with respect to nitrate reduction, but the initial negative impact would diminish quickly; for a long term operation, high TDS would not have any significant impact to the hZVI system. The self-adaptation of the hZVI media to a change in TDS might be attributed to the complex interactions between anions such as chloride and sulfate and the iron oxides during the ZVI corrosion process. The underlying mechanism(s) is yet to be clearly understood and warrants a more in-depth and detailed study in the future. Tests on the impact of dissolved silica and bicarbonate confirmed that dissolved silica has no significant impact on hZVI system reactivity, whereas bicarbonate may decrease the hZVI media reactivity and thus is more important factor. The tolerance of extreme TDS conditions by the hZVI system provides a major advantage to the hZVI technology over biological or conventional metal removal technologies in the application of many high strength industrial wastewater treatment.

Further studies on how high Mn^{2+} and Ni^{2+} could impact the hZVI system showed that hZVI media reactivity with respect to nitrate may be compromised when large quantities of Mn(II) and Ni(II) were removed from water and incorporated into FeOx structure. Various methods such as increasing media concentration and aeration etc, may slow down and temporarily alleviate the media passivation syndrome, the trend of decreasing reactivity with increased uptake of Mn(II) and Ni(II) would not be changed. For a wastewater with Mn^{2+} over 10 mg/L, it may be wise to remove Mn^{2+} through a pretreatment step before using the hZVI system to polish other main target contaminants for strict limit compliance. The presence of dissolved Fe^{2+} was found to interfere with Ni^{2+} removal by hZVI media. For a deep reduction of Ni^{2+}, the hZVI system should be operated under a Fe^{2+} deficient mode.

This study further expand our knowledge of the hZVI treatment system and extend its potential application scope to cover wastewater with extremely high concentration of total dissolved salts, Mn^{2+} and Ni^{2+}.

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